REACTIONS OF ALKYL RADICALS

BY

JAMES A. KERR, B.Sc.

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TO MY WIFE, NANCY.

ABSTRACT

The field of alkyl radical reactions has been reviewed. Most of the work, including results presented in this thesis, has been carried out in the gas phase, but where liquid phase studies have been made, they are included and compared with the results from the gas phase. Emphasis has been placed on quantitative experiments, and tables have been drawn up summarising the most reliable values of rate constants, rate constant ratios, Arrhenius parameters, etc., for the following classes of alkyl radical reaction: combination of like and unlike radicals; disproportionation; metathesis; addition to multiple bonds; and decomposition. Alkyl radical isomerisation has also been considered.

The photoinitiated chain decomposition of aldehydes has been extended and developed as a general method of studying the reactions of alkyl radicals. This has been possible by gas chromatographic analyses of the products. Quantitative information has been obtained by photolysing propionaldehyde, n-butyraldehyde, iso-butyraldehyde and n-valeraldehyde for ethyl, n-propyl, s-propyl and n-butyl radicals respectively, in reactions of all the above classes. By photolysing mixtures of aldehydes, the cross-combinations of ethyl with propyl and propyl with n-butyl radicals have been studied, and the results obtained, taken in conjunction with information in the literature, have led to general conclusions on alkyl radical combinations.

The cross-disproportionation reactions of methyl with s-propyl and t-butyl radicals have been investigated by photolysing mixtures of acetone with methyl iso-propyl ketone and pinacolone. The results of these studies considered with analogous information in the literature have been treated to yield information on the nature of the activated complex in a disproportionation reaction.

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PREFACE

Chapter I consists of a survey of the field of alkyl radical reactions, including the results of the work presented in the experimental sections of the thesis and could therefore be considered as a combined Introduction and Discussion. This is followed by a chapter on the general experimental technique, and the remaining chapters deal with the experimental results for the various radicals studied.

TABLE OF NOMENCLATURE

A = A factor
E = Activation energy
} Arrhenius parameters

$D(Y\text{-}Z)$ = Bond dissociation energy of bond Y-Z

$\Delta H(1)$ = Heat of reaction (1)

$\Delta H_f^\circ(X)$ = Heat of formation of substance X

k_1 = Rate constant of reaction (1)

R_X = Rate of formation of product X

$R_X(1)$ = Rate of formation of product X by reaction (1)

R = Alkyl radical

R = Gas constant

ΔS_1 = Entropy change of reaction (1)

T = Absolute temperature

$[X]$ = Concentration of X

CONTENTS

CHAPTER I

THE REACTIONS OF ALKYL RADICALS.

Until the end of the Second World War, the study of alkyl radical reactions in the gas phase was largely qualitative. The introduction of refined analytical techniques, such as low temperature distillation and mass spectrometry, however, made possible a quantitative approach. Naturally, workers in this field began by studying the reactions of the simplest alkyl radical, the methyl radical, and many results have been obtained for this radical.

At the start of the present study in 1956 our knowledge of the reactions of the higher alkyl radicals was fragmentary. Although ethyl radicals had been fairly extensively studied, information on propyl and higher radicals was lacking. Before more complete studies of these radicals could be initiated, two major problems had to be solved: (a) that of analysis of complex mixtures of hydrocarbons up to C_8 or more, and (b) the availability of suitable radical sources.

The first of these problems was almost completely solved by the development of gas chromatography (1955), but the second problem remained in 1956.

Section 1 of this chapter deals with the methods which have been used in the past to produce alkyl radicals, and the present approach to the problem.

1.1. RADICAL SOURCES

The Pyrolysis of metal alkyls as a source of alkyl radicals has been studied to quite a considerable extent[1], but mainly on a qualitative basis. The temperature conditions of most thermal reaction systems are unsuitable for the study of many of the radical reactions that are of interest. This restriction arises directly from the limited temperature range over which the systems can be used.

The Photolysis of metal alkyls has been a more successful method, particularly for the lower alkyl radicals. Although the mechanism is fairly complicated, the photolysis of dimethyl mercury is a reasonable source of methyl radicals. The advantages of acetone photolysis as a source of methyl radicals have, however, limited the exploitation of dimethyl mercury. Both dimethyl and diethyl mercury have been used as sources for their alkyl radicals, largely to corroborate the results obtained by ketone photolysis.

The higher metal alkyls are involatile and thermally unstable, so that they cannot readily be used in photochemical systems. Nevertheless, Caule and Steacie[2] have photolysed di-n-propyl mercury. The mechanism is complicated by heterogeneous thermal reactions, and there seem to be strong indications that the propyl radicals from this source are "hot", that is not in thermal equilibrium with their surroundings. Evidence also exists for "hot" radical formation in the photolysis of the lower mercury alkyls.

Moore and Wall[3] have photolysed di-n-butyl mercury, but, from the table of analytical products given, it is obvious that the mechanism is complex, and once again there is clearly evidence for "hot" radical formation.

Metal alkyls other than those of mercury have also provided sources of alkyl radicals[4], but again they have yielded qualitative results.

The Photolysis of Ketones. The mechanism of photolysis of

acetone is well established[5,6] and, using this source, the rates of many metathetical reactions of methyl radicals have been measured.[7] The mechanism of diethyl ketone photolysis has also been established with reasonable certainty, and for most purposes this is probably the best source of ethyl radicals.

Unfortunately, the photolysis of the higher ketones with α hydrogen atoms does not cleanly yield the expected radicals. Nicholson[8] has photolysed methyl-n-butyl ketone and confirmed the findings of Davis and Noyes[9] that the principal products from the primary process are acetone and propylene. Nicholson has also photolysed methyl n-propyl ketone, methyl iso-propyl ketone and methyl n-amyl ketone and shown that, except for methyl iso-propyl ketone, the primary processes are complicated by intramolecular rearrangements to give stable products.

Masson[10] has photolysed di-n-propyl ketone and shown that, as well as n-propyl radicals, ethylene and methyl n-propyl ketone are formed in considerable quantities in the primary process.

Since the quantum yields for the formation of products other than radicals are often high and the same products are produced by the reactions of the radicals themselves, their formation in the initial act considerably complicates the elucidation of the kinetics.

Quite recently, however, the photolysis of certain of the higher ketones has provided useful information on the reactions of alkyl radicals. Heller and Gordon[11] have shown that the photolysis of di-iso-propyl ketone yields almost entirely s-propyl radicals in the primary process.

Kraus and Calvert[12] have photolysed di-t-butyl, di-iso-butyl and di-s-butyl ketones. The di-t-butyl ketone photolyses cleanly to give t-butyl radicals and may prove a useful source for further study. The di-iso-butyl

ketone, as well as giving iso-butyl radicals, gives propylene in the primary process, and the di-s-butyl gives s-butyl radicals and ethylene. These sources have been used successfully to study the low temperature reactions of the alkyl radicals they yield (disproportionation and combination) although it is doubtful whether much information could be gleaned from higher temperature studies on di-iso-butyl and di-s-butyl ketones.

In the work presented in this thesis, methyl iso-propyl ketone has been used as a source of methyl and s-propyl radicals, and pinacolone (methyl t-butyl ketone) as a source of methyl and t-butyl radicals. The reactions studied here were low temperature processes, disproportionations and combinations, and only products of direct interest in this respect were analysed, so that very little can be said from this work on the primary processes in these photolyses, except that the corresponding alkyl radicals are produced to some extent.

In conclusion, then, it may be said that the photolyses of the higher ketones as sources of alkyl radicals may be satisfactory for low temperature studies, but are of limited application to high temperature processes.

Mercury Photosensitised Reactions. The mercury photosensitised decomposition of the paraffins has been extensively investigated as a source of alkyl radicals[13]. A serious disadvantage is that the parent molecules are the same as the products of some of the more interesting reactions of the radicals. Their presence prevents the measurement of these products. A further disadvantage is that the systems are not sources of a single radical species, though usually the secondary and tertiary radicals are produced in preference to the primary.

Nevertheless, until recently practically the only source of quantitative information on the decomposition of alkyl radicals was that

obtained by Bywater and Steacie[14], using the mercury photosensitised decomposition of the paraffins. Allowing for the disadvantages already pointed out, the results[15] obtained by Bywater and Steacie have largely been confirmed by recent work.

It is of interest to note that as yet the mercury photosensitised decomposition of ethane has been the only source used with success in a study of the ethyl radical decomposition. In this case, of course, only the one radical is produced.

It may also be possible to decompose neo-pentane in this way to give the neo-pentyl radical, which should be the only radical produced.

The only quantitative results reported so far for the reactions of cyclic alkyl radicals is the work of Gunning et al[16,17,18] on the mercury photosensitised decomposition of cyclopentane, methyl cyclopentane and cyclohexane. These results are for the rates of disproportionation relative to combination of the radicals involved.

The mercury photosensitised addition of hydrogen atoms to olefins has also been extensively investigated, although as a source of alkyl radicals it suffers from inherent disadvantages similar to those outlined for the mercury photosensitised decomposition of the paraffins. Since the addition of a hydrogen atom to an olefin is a highly exothermic reaction, the alkyl radicals produced are "hot"[19] and it is not surprising that the results for radicals produced in this way have often differed considerably from those of radicals which were in thermal equilibrium with their surroundings. This difficulty has partly been solved by the addition of inert gas to the system[20], but for the reasons previously given the method is generally of limited scope.

Azo Compounds. Azomethane has been pyrolysed and photolysed as a source of

methyl radicals. Similarly azoethane provides a source of ethyl radicals, but the azo compounds in general offer no advantages compared with ketone photolysis for methyl and ethyl radicals.

The only higher azo compound which appears to have been studied successfully is azo-iso-propane[21]. The photolysis of this compound has yielded results for the lower temperature reactions of s-propyl radicals. A temperature sufficiently high for s-propyl decomposition was not attained, presumably due to the onset of thermal reactions.

The preparation of the higher azo compounds is difficult, and no quantitative work has been reported on them.

Minor and Other Sources. Di-t-butyl peroxide has been used as a thermal source of methyl radicals. It has proved to be useful for studying metathetical reactions, where the nature of the substrate precludes photolysis. For instance, work is in progress in this laboratory on the abstraction of hydrogen atoms from aldehydes by methyl radicals using this source of the radicals.

A method it was hoped to develop consisted of generating radicals by means of a combined Sodium-Flame[22] Toluene-Carrier[23] technique. That is, by passing an acid chloride in a stream of toluene over sodium vapour, the following reaction should occur:

$$R\cdot COCl + Na = NaCl + R\cdot CO$$

and with subsequent decomposition of R·CO, the alkyl radicals would be expected to undergo normal Toluene-Carrier reactions. Although very little of the development work on this method was carried out by this author, it was found by Mr. R. N. Birrell of this laboratory that reproducible results could not be obtained.

Photolysis of Aldehydes. The primary processes in the photolysis of the

lower aldehydes are well established, due largely to the work of Blacet et al[24,112]. Although fragmentary information on the reactions of the alkyl radicals produced in the photolysis has been derived from these studies, it was not until the work of Gruver and Calvert[25] that an extensive study of an aldehyde photolysis was made for the primary purpose of studying the alkyl radical produced.

Gruver and Calvert photolysed 1-methyl butyraldehyde over a wide range of temperature to obtain information on the s-butyl radical.

This method has been used in the present work and by photolysing the corresponding aldehydes the following alkyl radicals have been studied, n-propyl, s-propyl, n-butyl and ethyl.

A detailed discussion of the primary processes in each of these photolyses will be left until later chapters, it being sufficient to say at this stage that as well as yielding the corresponding radicals, other stable products are produced in the primary act of photolysis of all four aldehydes.

However, due to the high metathetical reactivity of the hydrogen in the aldehydic group, a high proportion of the alkyl radicals will abstract this hydrogen atom,

$$R + R{\cdot}CHO = RH + R{\cdot}CO.$$

Subsequent decomposition of the R·CO regenerates an alkyl radical

$$R{\cdot}CO = R + CO.$$

Hence as the temperature is raised, the chains set up by these two reactions become increasingly long and the fact that the initial photolysis is not clean becomes decreasingly important. It is more correct then, to call this method the photoinitiated chain decomposition of aldehydes.

Furthermore, since most of the radicals are produced by the decomposition

of R'CO when the chains are long, the products formed by any excited radicals initially released may be disregarded.

This method is not, however, a suitable source of radicals for the study of metathetical reactions unless heavily deuterated substrates are present. This would make it possible to identify the products of the metathesis. The very high metathetical reactivity of the aldehyde makes it impossible to apply the treatment designed for ketonic sources[26].

Recently Calvert and Sleppy[27] have selectively photolysed azomethane at a wavelength of 3660 Å in n-butyraldehyde and studied the decomposition of the n-propyl radical in this system. However, due to the limited temperature range over which this selective photolysis may be carried out, the method is not of general applicability.

The reactions which the alkyl radicals derived from the above sources may undergo are: combination, disproportionation, metathesis, addition to double bonds and decomposition. The other sections in this chapter deal with these reactions.

1.2. COMBINATION REACTIONS.

Combination of Like Radicals. Although many alkyl radical combination reactions are known, few rate constants have been measured. The difficulty in making such a measurement lies in determining the concentration of radicals in any system. Since these concentrations lie far below the limits of normal analytical detection, they must be approached in most cases by an indirect method.

The method most commonly applied is that of the Rotating Sector or Intermittent Illumination. A full review of the method has been given by Melville and Burnett[28].

Basically it consists of determining the mean lifetime of the radicals and, knowing the rate of release of radicals into the system, the concentration is obtained. The lifetimes of radicals are measured by comparing the rate of disappearance of the radicals by reaction, with the rate of formation of the radicals by photolysis of their parent molecules, with light whose intensity varies with a period roughly equal to the lifetime of the radicals. In general the reaction mechanism must be very clearly defined before the Rotating Sector technique can be applied.

Methyl Radicals. Gomer and Kistiakowsky[29] have applied the Rotating Sector method successfully to determine the rate constant for combination of methyl radicals produced in the photolysis of acetone and dimethyl mercury. The agreement between the results for the rate constant (k_c) of the combination of methyl radicals from the different radical sources was very good.

The value which Gomer and Kistiakowsky put forward was

$$k_c = 10^{13\cdot65} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

with an activation energy of $E = 0 \pm 700$ cal.mole^{-1} between 125 and 220°C., and a total pressure in the system of between 10 and 50 mm.

This value was revised by Kistiakowsky and Roberts[30], after further studies on the photolysis of acetone, to

$$k_c = 10^{13.57} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at 165°C. and a pressure of 30 mm. of acetone. A similar value was obtained in the same work for the rate constant for the combination of trideuteromethyl radicals.

More recently, Shepp[31] has improved the theory of the Rotating Sector technique and he calculates the value of the rate constant from the results of acetone photolysis[29,30] to be

$$k_c = 10^{13.34} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

in the temperature range 125 to 175°C. This is the currently accepted value.

The photolysis of acetaldehyde has also been used in studies of methyl radical combination by the Rotating Sector[32,33,34] method. Although the values of the rate constant for methyl radical combination from this source agree fairly well with those from acetone photolysis, this is perhaps fortuitous, since there is considerable doubt concerning the mechanism. In these investigations on the photolysis of acetaldehyde the reaction was followed by pressure change in a static system. Perhaps a study involving analysis of the products would be more useful.

Another method for measuring radical concentrations, and hence rate constants for combination reactions, consists of introducing the radicals, produced by pyrolysis in a flow system, directly into the ionisation chamber of a mass spectrometer. In practice, the flow system is usually connected to the mass spectrometer via a pin hole leak in a quartz thimble. This method has been applied to measure the rate of methyl radical combination in various

pyrolytic systems. Lossing, Ingold and Tickner[35,36] determined the rate constant for methyl combination to be

$$k_c = 10^{12.71} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at 850 to 975°C., with a pressure of about 15 mm. of helium carrier gas and only a few microns of organic vapour. Ingold and Lossing[37], refining this technique, reported that, upon reducing the temperature to 160°C., the rate constant rose to about

$$k_c = 10^{13.11} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

Here again there is reasonable agreement with the rate constant from acetone photolysis by the Rotating Sector method.

Moseley and Robb[38] have recently developed another method for the direct determination of rate constants of radical-radical reactions. Measurements are recorded by observing the pressure change occurring in the gas resulting from the adiabatic temperature changes caused by reaction. The pressure changes are observed by means of a sensitive diaphragm type manometer, whose sensitivity in detection is better than 10^{-4} mm. Hg., and whose time lag in response is less than 10^{-3} second. The reaction studied by this technique was the photolysis of acetone and the rate constant for methyl radical combination found to be

$$k_c = 10^{13.60} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at room temperature and total acetone pressure of 75 mm.

The results from the three totally different studies for the rate constant for methyl radical combination are in good agreement, considering the experimental difficulties in determining this rate constant by any method, and

the wide range of experimental conditions over which the measurements were made. For the purpose of presenting other results, such as metathesis involving methyl radicals, it therefore seems justifiable to accept the value put forward by Shepp[31] for the rate constant of methyl radical combination.

The combination of the analogous trifluoromethyl radical has been studied by Ayscough[39] by the Rotating Sector method, with hexafluoroacetone as a source of radicals.

A rate constant for trifluoromethyl radical combination of

$$k_c = 10^{13\cdot36} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at 127°C was determined at a pressure of about 40 mm. of hexafluoroacetone.

Ethyl Radicals. Ivin and Steacie[40] have determined the rate constant for ethyl radical combination by photolysing diethyl mercury in Rotating Sector experiments. The value which may be calculated from their work[41] for the rate constant is

$$k_c = 10^{13\cdot20} \exp.(-\langle 700/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at a pressure of 80 mm. of diethyl mercury. A more complete study on the Rotating Sector photolysis of diethyl ketone has been carried out by Shepp and Kutschke[42], who found the value of the rate constant for ethyl combination to be

$$k_c = 10^{14\cdot48} \exp.(-2000\pm1000/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at diethyl ketone pressures of 10 to 50 mm., which is in reasonable agreement with the previous determination.

n-Propyl Radicals. Whiteway and Masson[43] have determined the rate constant for combination of n-propyl radicals by Rotating Sector photolysis of di-n-propyl ketone to be

$$k_c = 10^{15\cdot78} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at 100°C. and a ketone pressure of about 12 mm. This value is much higher than those measured for other alkyl radical combinations, and indeed the authors estimate that it may be high by a factor of 20.

Little reliance, then, should be placed on this determination, since it seems that the mechanism of di-n-propyl ketone photolysis is not well enough understood for a rotating sector experiment to be applied.

Large Alkyl Radicals. No work has been reported on the rates of combination of alkyl radicals higher than n-propyl. In the work presented in later parts of this thesis, where radical concentrations were measured in terms of the rate of formation of the dimer, it was convenient for the purposes of presenting results, to select arbitrary values of the Arrhenius parameters for the combination reactions of n-propyl, s-propyl and n-butyl radicals. The values which were chosen are

$$E = 0 \text{ k.cal. mole}^{-1} \quad \text{and} \quad A = 10^{14.0} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

All the results listed above indicate that the activation energy for an alkyl radical combination is very low. This is what one might intuitively expect.

The A factor of $10^{14.0}$ mole^{-1} cm.^{3} sec.$^{-1}$ may be out by one or two powers of ten, but when these rate constants are determined it will be a comparatively simply matter to rescale the results presented here.

For the purposes of comparison the same parameters were chosen for ethyl radical combination, although these have been determined experimentally.

Radical Combination and the Effect of Pressure. Since methyl radicals contain only one heavy atom, it is possible that the rate of methyl radical combination may be markedly dependant upon pressure, due to third body effects. These effects are well known in atomic combinations and in the case of methyl radicals it would be expected that the rate constant for combination should

decrease with decreasing pressure. Marcus and Rice[44,45] have considered this effect and conclude that the energy effects should become important for methyl radical combination in the pressure region of a few millimeters.

The first attempts to detect this falling off in the rate constant were not conclusive[46,47,48] but Kistiakowsky and Roberts[30] found that the rate constant for the combination of methyl radicals falls to about one-third of its high pressure value when the total pressure in the system is reduced to 1 mm. This is in good agreement with Marcus's prediction. This finding has been confirmed by the work of Dodd and Steacie[49] on the photolysis of acetone at pressures down to 0·2 mm. They also showed that the rate constant for methyl combination at very low acetone pressure was increased by the presence of added inert gases, owing to third body effects.

One would expect any pressure dependence in the rate of combination of ethyl radicals to be much less than that for methyl radicals. This has been confirmed by Brinton and Steacie's[50] work on the photolysis of diethyl ketone. They have shown that although there is definite evidence for third body effects in the combination of ethyl radicals they are decidedly less than for methyl radical combination. A quantitative study of this effect for ethyl radicals was not possible owing to complications in the mechanism of diethyl ketone photolysis.

Since the number of degrees of freedom in large alkyl radicals is considerable one would not expect there to be pressure effects in their combination reactions.

Radical Combination and Transition-State Theory. On the basis that there is a considerable loss of rotational entropy when two alkyl radicals combine, the value of the A factor for a bimolecular combination which may be calculated

from transition-state theory, is about 10^{11} mole^{-1} cm.^{3} sec.$^{-1}$.

From the results quoted in the first part of this section, it may be seen that the experimental values of A factors for bimolecular combinations approach $10^{14\cdot3}$ mole^{-1} cm.^{3} sec.$^{-1}$, the collision rate.

However, these findings may be explained by supposing that the radical fragments rotate freely in the activated complex. No rotational entropy is then lost when the complex is formed. Thus, the radicals behave like atoms, which have no rotational entropy to lose.

COMBINATION OF UNLIKE RADICALS. Three combination reactions can occur in a system containing two different alkyl radicals, A and B,

$$2A = A_2 \;..\;..\; k_{aa}$$
$$2B = B_2 \;..\;..\; k_{bb}$$
$$A + B = AB \;..\;..\; k_{ab}.$$

According to the simple collision theory of chemical kinetics, the ratio $k_{ab}/(k_{aa}\,k_{bb})^{\frac{1}{2}}$ should equal 2 if none of the reactions has an activation energy. It has long been known that the reactions that terminate polymerisations and autoxidations in solution deviate from this simple relation. Recently several measurements of the ratio have been reported for gaseous systems, and further information may be deduced from other published results(f).

These results are summarised in Table 1.1. which may be augmented by a few notes on the means by which the results were obtained.

Notes:-

(i) This figure was calculated from the results on the photolysis of methyl ethyl ketone below 170°C. The amount of ethane by methyl combination was calculated from the yield of methane and from the rate constant for attack of methyl radicals on the ketone. This constant had been found by photolysing

TABLE 1.1. COMBINATION OF UNLIKE RADICALS

Radicals A	Radicals B	$k_{ab}/(k_{aa}\,k_{bb})^{\frac{1}{2}}$	Reference	Note
Methyl	Trideuteromethyl	1·9	56	
Methyl	Ethyl	1·9	51	(i)
		2.0	52	
Trideuteromethyl	Ethyl	1·8	53	
Methyl	n-Propyl	2·6	54	(ii)
		1·4	55	(iii)
		2·1	8	
Methyl	Acetyl	1·7	56	
Methyl	Acetonyl	1·5	57	(iv)
Ethyl	n-Propyl	1·9	(a)	
Ethyl	s-Propyl	2·0	(b)	
		2	58	(v)
Ethyl	n-Heptafluoropropyl	3·2	59	(vi)
Ethyl	Pentanonyl	1·7	50	
n-Propyl	n-Butyl	2·0	(c)	
s-Propyl	n-Butyl	2·2	(c)	

azomethane with the ketone.

(ii) This result is based on a few runs which were not very concordant; the limits of error are large.

(iii) In this reaction system, where the addition of methyl radicals to ethylene was the primary consideration, the low value of the ratio of rate constants is undoubtedly due to the formation of n-hexane by a source other than the combination of two n-propyl radicals.

(iv) The authors reported very scattered results that showed no trend but the error limits were between 1·0 and 2·5.

(v) This result has been calculated from the yields of n-butane, iso-pentane and 2:3-dimethyl butane formed in the photolysis of iso-propyl propionate.

(vi) Calculated from the yields of n-butane, and n-1:1:1:2:2:3:3-heptafluoropentane. The yield of perfluorohexane was estimated as was done by the original authors for the photolysis of di-n-perfluoropropyl ketone in the presence of ethane. The figures are rather scattered.

None of these ratios vary with temperature. Only the ratio involving perfluoropropyl radicals differs significantly from the expected value of two and its deviation is smaller than might have been expected for such a polar radical. The results must therefore be regarded as an indication, though not as a proof, that all these combinations occur on every collision. It is probable, however, that the collision diameter required for the present purpose is generally slightly different from that required for the calculation of transport properties as it is known to be for the combination of two methyl radicals.[31]

1.3. DISPROPORTIONATION REACTIONS.

When two alkyl radicals react they may combine or disproportionate:

$$R + R = R_2 \quad .. \quad .. \; k_c$$

$$R + R = RH + r \quad .. \quad .. \; k_d$$

where R_2 is a dimer, RH is a paraffin and r is an olefin. Since disproportionations involve the transfer of a hydrogen atom from one radical to another, they could be classified as metathetical reactions. Usually, however, since they have very small activation energies, disproportionations are considered separately with combinations. The small activation energies are due to the high exothermicity of disproportionation reactions, arising from the formation of the olefin product. For instance, the autodisproportionations of ethyl, n-propyl and s-propyl radicals are exothermic to the extent of 58, 64 and 54 k.cal. whereas normal metathetical reactions are only some 0 to 25 k.cal.

exothermic.

When two different alkyl radicals are present in a system, as well as combining with each other, they may disproportionate. These reactions are sometimes called cross-combinations and cross-disproportionations and as with combinations it will be convenient to consider them separately.

Disproportionations involving the transfer of atoms other than hydrogen have not so far been studied quantitatively. Dainton, Lomax and Weston[61] produced the tetrachloro-ethyl radical by photochlorination of trichloroethylene and have postulated a disproportionation involving chlorine atom transfer. It is also interesting to note that although the perfluoro-n-propyl radical does not undergo autodisproportionation between 25 and 250°C.[62] it will cross-disproportionate with alkyl radicals to abstract a hydrogen atom[59].

DISPROPORTIONATION OF LIKE RADICALS.

From the equations above it follows that

$$R'_{R_2} = k_c[R]^2$$

and $$R'_{RH} = R'_r = k_d[R]^2$$

where R'_X = rate of formation of X

$$\therefore \quad k_d/k_c = R'_{RH}/R'_{R_2} = R'_r/R'_{R_2}.$$

Thus disproportionations may be followed by measuring the rate of formation of the paraffin or olefin and the rate of formation of the dimer. Usually, since the paraffin is produced by other reactions of the radicals, it is more convenient to use the rate of formation of the olefin. This is not the case when the source of radicals is the addition of hydrogen atoms to olefins, where the presence of the parent molecule necessitates following the reaction by the rate of formation of the paraffin.

Only in one instance has the rate constant for disproportionation been determined absolutely. The rate of disproportionation of ethyl radicals released by the photolysis of diethyl mercury was found to be given by[40]

$$k_d = 10^{13.51} \exp.(-800/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

This value is based on the rate constant for ethyl combination obtained by Shepp and Kutschke[42].

Table 1.2. gives a summary of the results which have been obtained for the ratio k_d/k_c. In the cases where numerous investigations have been carried out only values which appear to be most reliable have been included.

A striking feature of the table is that for the same radical, remarkably different values of k_d/k_c have been found. However, the situation becomes less complicated when one considers the results obtained from sources producing radicals which are in thermal equilibrium with their surroundings and results from sources which produce radicals with excess energy.

Hence it may be seen that the results from aldehyde and ketone photolyses (thermally equilibrated radicals) are in excellent agreement. On the other hand, results from the mercury photosensitised addition of hydrogen atoms to olefins or the photolysis of metal alkyls, are usually considerably different from those from aldehyde or ketone photolyses.

It therefore seems reasonable to accept the values derived from aldehyde or ketone photolyses as being the most reliable.

No complete theory has been put forward to account for these values, but, however, a few interesting points have arisen.

The hydrogen atom which is transferred in the disproportionation of an ethyl radical has been identified, by the photolysis of 2:2:4:4-tetradeutero-diethyl ketone[63,64]. The products from the reactions of the CH_3CD_2 radicals

contained more than 90% of $CH_2=CD_2$, so that in a disproportionation the radicals must react by a head to tail mechanism, to give the following activated complex:-

$$CH_3\ CD_2 - H - CH_2\ CD_2$$

and not by a head to head mechanism which would be expected if an excited butane molecule took part in the disproportionation and which would lead to the formation of $CD_2=CD_2$.

Ausloos and Steacie[51] made the interesting observation that the assumption of the equality of the rate constants for the combination reactions involving s-propyl and n-propyl radicals, leads to a semiquantitative prediction of the rate constants for the disproportionation of these radicals, based on the number of hydrogen atoms available for disproportionation in each radical.

Kraus and Calvert[12] later found that the ratio k_d/k_c bears a simple relationship to the number of abstractable hydrogen atoms available for disproportionation in the case of the butyl radicals, as may be seen from the table below.

Radical	k_d/k_c	$a.k_d$	No. of abstractable H atoms
t - C_4H_9	$4{\cdot}5_9$	10·1	9
iso - C_4H_9	$0{\cdot}41_8$	0·92	1
s - C_4H_9	$2{\cdot}2_7$	5·0	5

Column 3 of the table shows the relative values of k_d, normalised so that $a.k_d$ for the s-butyl radical is equal to 5·0 and assuming that the rate constants for the combination reactions of the butyl radicals are equal.

Calvert concluded that the dominant factor which determines the rate of the disproportionation reaction of butyl radicals is the number of abstractable

hydrogen atoms which can be removed from the radical to form a stable olefin product, provided, of course, that the rate constants for butyl combinations are equal.

On the basis of the above results Kraus and Calvert predicted that k_d/k_c for n-butyl radicals would be about 0·9 at 100°C. The value of 0·7 obtained from the photolysis of n-valeraldehyde[c] at 100°C. is significantly different, although its position relative to the other butyl radicals is correct.

No temperature coefficient has been found in the disproportionation-combination reactions of ethyl, n-propyl or s-propyl radicals. It is surprising, therefore, that a considerable temperature coefficient has been found for n-butyl radicals[c]. The rate constant for disproportionation of this radical is given by

$$k_d = 10^{14\cdot6} \exp.(-1300/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1},$$

if the rate of combination is given by

$$k_c = 10^{14\cdot0} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

In the past, such temperature coefficients have usually vanished in the light of improved experimental technique, but in this case the method employed gave results which were in excellent agreement with those obtained for ketone photolysis for ethyl, n-propyl and s-propyl radicals. The authors therefore believe this temperature coefficient to be real. Bradley, Melville and Robb[20] have shown that the ratio k_d/k_c is dependent on the energy content of the radicals. By photolysing diethyl mercury they found k_d/k_c for ethyl radicals to be 0·344 at a pressure of 20 mm. of neon but only 0·054 at 200 mm. of neon. This effect is not understood, and it seems that if any advance is to be made in understanding why disproportionation-combination rate constant ratios have the values they do, it must stem from studies of radicals in thermal equilibrium with their surroundings.

The disproportionations discussed above all yield as products a paraffin and an olefin. There is no reason, however, why the products should not be an alkane and a substituted methylene. Such a reaction may well be exothermic though not so exothermic as a normal disproportionation and have a very low activation energy. The only known example of this kind of reaction is that of the acetonyl radical[70],

$$2CH_3 \cdot CO \cdot CH_2 = CH_3 \cdot CO \cdot CH_3 + CH_3 \cdot CO \cdot CH .$$

DISPROPORTIONATION OF UNLIKE RADICALS.

It will be convenient to define the ratio of rate constants for disproportionation to combination k_d/k_c as $\triangle$:

$\triangle$ (Me, Et) refers to the reactions

$$CH_3 + C_2H_5 = CH_4 + C_2H_4$$

and $$CH_3 + C_2H_5 = C_3H_8$$

and $\triangle$ (n-Pr, Et) to the reactions

$$C_3H_7 + C_2H_5 = C_3H_8 + C_2H_4$$

$$C_3H_7 + C_2H_5 = C_5H_{12}.$$

Recently a series of values of $\triangle$ (Alk, Alk) for different alkyl radicals have been reported, as given in Table 1.3. The values which have been obtained for radicals which are thermally equilibrated lead to interesting theoretical findings.

It has been found that:

$\triangle$ (Me, Et) = 0·06

$\triangle$ (Me, s-Pr) = 0·22

$\triangle$ (Me, t-Bu) = 0·70

and these values bear a simple relation to those of $\triangle$ (Alk, Alk). In an ethyl radical there are three hydrogen atoms available for removal by disproportionation,

whereas in s-propyl there are six, and in t-butyl nine. The values of Δ may be simply reduced to the same standard by division by the number of available hydrogens with the result shown in Table 1.4. and Figure 1.1. The plot of log Δ (Me, Alk) against log Δ (Alk, Alk) is a good straight line, though much importance should not be attached to this fact because there are only three points comparatively close together and the experimental errors are considerable. The fact that the slope is close to one-half (0·55) is of greater significance. It implies that the same factors that make t-butyl lose a hydrogen atom readily also make it equally ready to acquire a hydrogen atom. This does not involve a contradiction but it is surprising because it implies that t-butyl abstracts a hydrogen atom more readily than ethyl which forms a stronger C-H bond. The matter may be tentatively taken one step further by suggesting that the slope of one-half indicates that in the activated complex it is not certain which of the two t-butyl radicals is to lose and which to gain a hydrogen atom. This might occur if the radicals in the complex were loosely held together but rotated freely. It has been possible to explain the absolute A factors for the combination of alkyl radicals only by assuming complexes of this type (see Chapter 1.2.).

An extensive study of cross-disproportionations has recently been published by Boddy and Robb[67], who used the mercury photosensitised addition of hydrogen atoms to olefins as a source of alkyl radicals. The Δ (Alk, Alk) values obtained with ethyl and s-propyl did not agree very well with those from aldehyde or ketone photolyses and the value for t-butyl did not agree at all. Further, these Δ (Alk, Alk) values had to be used to determine the cross-disproportionation values. It is not surprising that the results do not show the regularity exhibited by those mentioned above from ketone or aldehyde photolyses.

More information on cross-disproportionations must be obtained before

the properties of the activated complexes can be deduced with certainty. It is hoped that the photolyses of mixtures of aldehydes will be a fruitful source of such information.

TABLE 1.2. DISPROPORTIONATION OF LIKE RADICALS

Radicals and Source	Temperature (°C.)	k disproportionation / k combination	Reference
ETHYL RADICALS			
Diethyl ketone P	100 - 250	0·12	50
	180 - 230	0·14	65
2:2:4:4-Tetradeutero diethyl ketone P	24 - 180	0·1	63
Propionaldehyde P	50 - 315	0·15	(e)
Diethyl mercury P	75 - 200	0·42	40
T	350	0·13	66
Ethylene + H	20	0·1	67
	20	0·15	68
n-PROPYL RADICALS			
Di-n-propyl ketone P	100 - 150	0·13	43
n-Butyraldehyde P	25 - 190	0·16	(a)
Di-n-propyl mercury P	30 - 108	0·3	2
s-PROPYL RADICALS			
Di-iso-propyl ketone P	25 - 150	0·63	11
iso-Butyraldehyde P	20 - 260	0·65	(b)
Azo-iso-propane P	30	0·53	21
Di-iso-propyl mercury T	230 - 440	1	69
Propylene + H	20	0·5	67
n-BUTYL RADICALS			
n-Valeraldehyde P	100	0·7	(c)
Di-n-butyl mercury P	140	1·5	3
iso-BUTYL RADICALS			
Di-iso-butyl ketone P	100	0·42	12
1-Butene + H	24	1·5	3
	220	3·5	
s-BUTYL RADICALS			
Di-s-butyl ketone P	100	2·27	12
2-Butene + H	20	1·5	67
t-BUTYL RADICALS			
Di-t-butyl ketone P	100	4·59	12
iso-Butene + H	20	2·2	67

TABLE 1.2. (continued)

Radicals and Source	Temperature (°C.)	$\frac{k \text{ disproportionation}}{k \text{ combination}}$	Reference
CYCLOPENTYL RADICALS			
Cyclopentane - H	30	0·2	16
METHYL CYCLOPENTYL RADICALS			
Methyl cyclopentane - H	30	0·4	17
CYCLOHEXYL RADICALS			
Cyclohexane - H	30	0·5	18

P Radicals produced by photolysis of parent compound.

T Radicals produced by thermal decomposition of parent compound.

+ H Radicals produced by mercury photosensitised addition of hydrogen to olefins.

- H Radicals produced by mercury photosensitised decomposition of paraffins.

TABLE 1.3. DISPROPORTIONATION OF UNLIKE RADICALS

Radicals and Source	Temperature (°C.)	Δ (Alk,Alk)	Reference
METHYL RADICALS i.e. Δ (Me, Alk)			
Alk.-			
ETHYL			
Methyl ethyl ketone P	25 - 240	0·04	51
Acetone + 2:2:4:4-Tetradeutero diethyl ketone P	90	0·06	52
s-PROPYL			
Acetone + Methyl iso-propyl ketone P	80 - 150	0·22	(a)
t-BUTYL			
Acetone + Pinacolone P	80 - 190	0·70	(a)
METHOXYL			
Methyl acetate P	30 - 90	1·4	56
ETHYL RADICALS i.e. Δ (Et, Alk)			
Alk.-			
s-PROPYL			
Ethylene + Propylene + H	20	0·4	67
t-BUTYL			
Ethylene + iso-Butene + H	20	0·6	67
s-PROPYL RADICALS i.e. Δ (sPr, Alk)			
Alk.-			
ETHYL			
Propylene + Ethylene + H	20	0·6	67
s-BUTYL			
Propylene + 2-Butene + H	20	0·8	67
t-BUTYL			
Propylene + iso-Butene + H	20	1·0	67
s-BUTYL RADICALS i.e. Δ (s-Bu, Alk)			
Alk.-			
s-PROPYL			
2-Butene + Propylene + H	20	0·8	67
t-BUTYL			
2-Butene + iso-Butene + H	20	0·5	67

TABLE 1.3. (continued)

Radicals and Source	Temperature (°C.)	Δ(Alk,Alk)	Reference
t-BUTYL RADICALS i.e. Δ(t-Bu, Alk)			
Alk.-			
ETHYL			
iso-Butene + Ethylene + H	20	3·4	67
s-PROPYL			
iso-Butene + Propylene + H	20	2·4	67
s-BUTYL			
iso-Butene + 2-Butene + H	20	4·0	67
PERFLUORO n-PROPYL RADICALS i.e. Δ(C_3F_7, Alk)			
Alk.-			
ETHYL			
Perfluoro n-propyl ketone + Ethane P	100 - 180	0·4	59

TABLE 1.4.

Radical	Available H atoms	Δ(Me,Alk)	$\frac{\Delta(\text{Me,Alk})}{\text{H}}$	Δ(Alk,Alk)	$\frac{\Delta(\text{Alk,Alk})}{\text{H}}$
Et	3	0·06	0·02	0·13	0·043
s-Pr	6	0·22	0·036	0·64	0·11
t-Bu	9	0·70	0·078	4·6	0·51

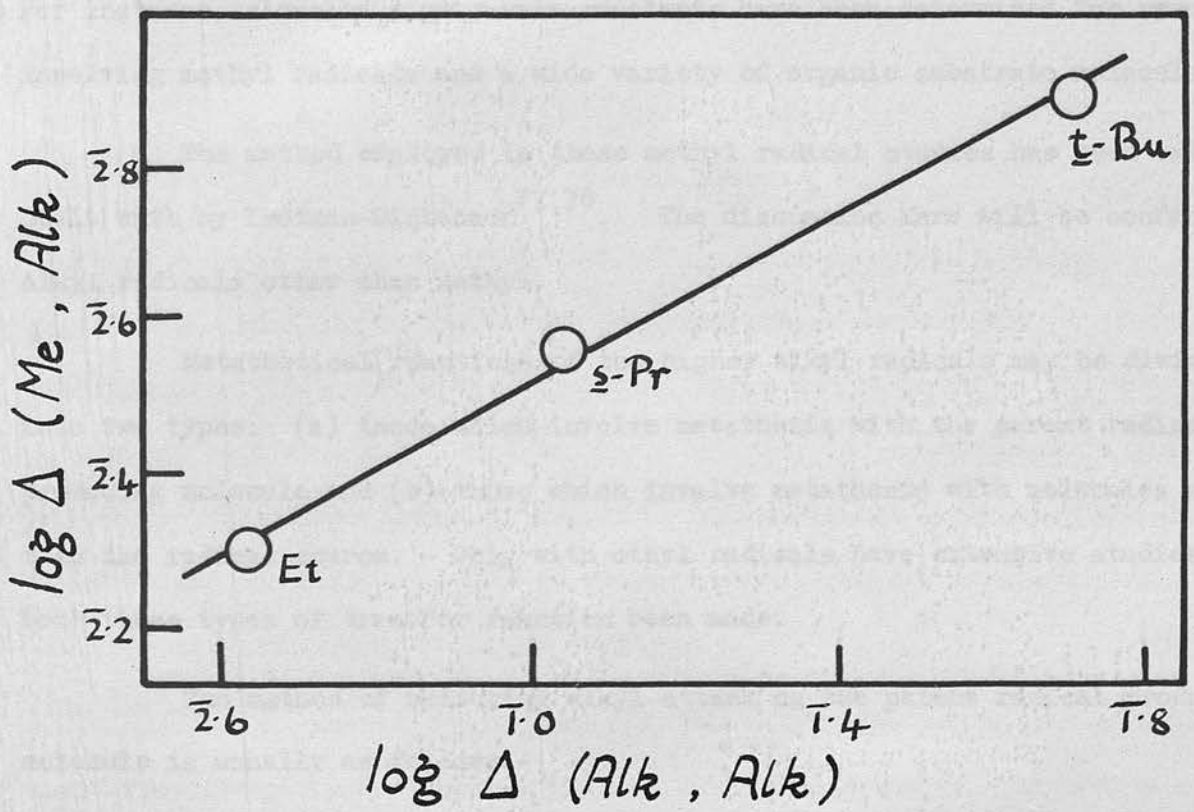


Fig. 1.1. The relation between the rates of cross-disproportionation with methyl radicals and auto-disproportionation for ethyl, s-propyl and t-butyl radicals.

1.4. METATHETICAL REACTIONS

The only type of metathetical reaction which has been studied quantitatively for alkyl radicals is that which involves the transfer of a hydrogen atom:

$$R + HX = RH + X.$$

This is undoubtedly the most widely studied class of alkyl radical reactions. For instance, close on eighty rate constants have been determined for reactions involving methyl radicals and a wide variety of organic substrate molecules.

The method employed in these methyl radical studies has been extensively dealt with by Trotman-Dickenson[77,78]. The discussion here will be confined to alkyl radicals other than methyl.

Metathetical reactions of the higher alkyl radicals may be divided into two types: (a) those which involve metathesis with the parent radical producing molecule and (b) those which involve metathesis with molecules other than the radical source. Only with ethyl radicals have extensive studies of both these types of transfer reaction been made.

The method of measuring alkyl attack on the parent radical producing molecule is usually as follows:-

The general reaction scheme is

$$\text{Radical Source} = R$$

$$2R = R_2 \qquad (1)$$

$$2R = RH + \text{olefine} \qquad (2)$$

$$R + \text{Radical Source} = RH + \text{other radical.} \qquad (3)$$

A photolytic source of radicals is most commonly employed. R_2 is the radical dimer; RH is a paraffin. As in any large alkyl radical system we have combination (1) and disproportionation (2). The question is to measure the rate constant of reaction (3).

From the above scheme it follows that the rate of formation of the paraffin is equal to $R_{RH}(2)$ plus $R_{RH}(3)$, where $R_{RH}(2)$ is the rate of formation of the paraffin from reaction (2). Since $R_{RH}(2)$ is equal to $R_{olefin}(2)$ and in most systems this is the only source of the olefin, by measuring its rate of formation, $R_{RH}(2)$ may be found. Hence $R_{RH}(3)$ is obtained by subtraction. Now, from reaction (1) it may be shown that

$$[R] = R_{R_2}^{\frac{1}{2}}/k_1^{\frac{1}{2}}$$

and from (3)

$$k_3 = R_{RH}(3)/[R][\text{Radical Source}]$$

$$\therefore\ k_3/k_1^{\frac{1}{2}} = R_{RH}(3)/[\text{Radical Source}]\ R_{R_2}^{\frac{1}{2}}.$$

[Radical Source] is the concentration of the parent molecule, which may be regarded as remaining constant for small percentage conversions, or which is a mean value. Thus, the rate constant for hydrogen abstraction (k_3) may be determined in terms of the rate constant (k_1) for the combination of the radicals. By either assuming reasonable values of the parameters for radical combination, or using experimental values where these are available, it is possible to obtain parameters for reaction (3).

In the case of ethyl radicals, where hydrogen abstractions from substances other than the radical source have been measured, the source of the radicals is the photolysis of diethyl ketone. The mechanism is well established[65]:

$$C_2H_5{\cdot}CO{\cdot}C_2H_5 + h\nu = 2C_2H_5 + CO$$

$$2C_2H_5 = C_4H_{10} \qquad (4)$$

$$2C_2H_5 = C_2H_6 + C_2H_4 \qquad (5)$$

$$C_2H_5 + (C_2H_5)_2CO = C_2H_6 + C_2H_4{\cdot}CO{\cdot}C_2H_5 \qquad (6)$$

$$C_2H_5 + C_2H_4{\cdot}CO{\cdot}C_2H_5 = C_4H_9{\cdot}CO{\cdot}C_2H_5. \qquad (7)$$

Reaction (7) occurs at higher light intensities and at temperatures below 250°C. The material balance derived from this scheme and checked experimentally is exceptionally good, thus confirming the mechanism.

From the above reaction scheme it may be shown that

$$k_6/k_4^{\frac{1}{2}} = \frac{R_{C_2H_6} - R_{C_2H_4}}{\left[(C_2H_5)_2\cdot CO\right] R_{C_4}^{\frac{1}{2}}}$$

$$= \left(\frac{R_{C_2}}{R_{C_4}} - \frac{2k_5}{k_4} \right) \frac{R_{C_4}^{\frac{1}{2}}}{\left[(C_2H_5)_2\cdot CO\right]} .$$

The value of k_5/k_4, in this experiment, has been found to be constant at 0·14, independent of temperature or ketone pressure. Hence the rate constant k_6 derived in the above manner has been found with reasonable certainty.

If the photolysis is carried out in the presence of a substrate molecule RH, which contains abstractable hydrogen atoms, reaction (8) occurs in addition to those above:

$$C_2H_5 + RH = C_2H_6 + R \qquad (8).$$

Provided that the resulting radical R does not lead to C_2 or C_4 products, we have for reaction (8)

$$k_8/k_4^{\frac{1}{2}} = \left(\frac{R_{C_2}}{R_{C_4}} - \frac{2k_5}{k_4} \right) \frac{R_{C_4}^{\frac{1}{2}}}{[RH]} - \frac{\left[(C_2H_5)_2\cdot CO\right]}{[RH]} \frac{k_6}{k_4^{\frac{1}{2}}} .$$

The results obtained in this way are listed in Table 1.5.

Trotman-Dickenson[79] has suggested another method for studying the metathetical reactions of ethyl radicals, involving a deuterated ketone radical source. Since the rate of abstraction of the secondary deuterium atoms in 2:2:4:4-tetradeuterodiethyl ketone is so much faster than the rate of abstraction of the primary atoms, this partially deuterated ketone, which is comparatively easily prepared, may be used instead of the fully deuterated compound. When photolysis is carried out in the presence of a substrate molecule RH, we have

$$C_2H_3D_2 + RH = C_2H_4D_2 + R \quad (9)$$

$$C_2H_3D_2 + (CH_3CD_2)_2{\cdot}CO = C_2H_3D_3 + CH_3CD{\cdot}CO{\cdot}CD_2CH_3. \quad (10)$$

Here again a correction for ethane ($C_2H_3D_3$) by disproportionation would have to be applied, and allowing for this, it follows from equations (9) and (10) that

$$k_9/k_{10} = R_{C_2H_4D_2}\left[(C_2H_5)_2{\cdot}CO\right] / R_{C_2H_3D_3}\left[RH\right]$$

and k_9 could thus be determined.

General Features of Metathetical Reactions of Alkyl Radicals. As previously mentioned, the most complete study of metathetical reactions is that of methyl radical hydrogen abstractions. The overall picture presented by these results has raised some interesting points.

In general, it has been found that for any particular group of organic substrates the methyl radical will abstrate tertiary hydrogen atoms faster than secondary, and secondary faster than primary. This finding has also been observed in the liquid phase. Buckley and Szwarc[80] have shown, by studying the abstraction of hydrogen atoms in alkenes by methyl radicals in iso-octane solution, that the rate constants for active hydrogen (α to C=C) fall into three distinctive classes characterising the primary, the secondary and the tertiary atoms.

Reference to the table drawn up by Trotman-Dickenson[78] shows that the spread of activation energies for methyl radical abstractions, over a wide range of substrates, is small, only 8k.cal. mole^{-1}. Little progress has yet been made in the calculation of absolute activation energies of metathetical reactions. However, it was suggested by Polanyi that the heat of one reaction in a series and its energy of activation may be related. Where there is no resonance stabilisation in the transition complex, or a constant amount of stabilisation throughout a series of metathetical reactions, the relationship

is

$$E = \alpha H + \text{constant}$$

where E is the activation energy, H the heat of the reaction and α has a value between 0 and 1. On this basis Trotman-Dickenson[81] proposed a relationship between the activation energies for the metathetical reactions of methyl radicals with alkanes and the strengths of the relevant C-H bonds. He obtained the straight line relationship

$$E = 12{\cdot}5 + 0{\cdot}5\ H$$

but the C-H bond strengths were estimated by a questionable procedure[82]. Dainton, Ivin and Wilkinson[83] later extended this treatment but did not obtain a straight line relationship between the activation energies for a series of methyl radical abstractions and the heats of the reactions.

The experimentally derived A factors for the hydrogen abstraction reactions of methyl radicals lie close to 10^{11} mole^{-1} cm.^{3} sec.$^{-1}$. Estimates from transition-state theory of A factors for methyl radical and analogous trideutero and trifluoro methyl radical abstraction reactions from hydrocarbons agree well with experimental values[84,85]. However accurate estimates of the A factors of the reactions of large alkyl radicals cannot be made from transition-state theory. This is because the size barrier to free rotation in the activated complex is not known, and hence the entropy associated with internal rotation of a large group, which is considerable, cannot be estimated with certainty. Errors in this estimate considerably affect the value of the A factor.

In comparison with methyl radicals, very few studies on the metathetical reactions of the higher alkyl radicals have been reported. The work of James and Steacie[65] on the hydrogen abstraction reactions of ethyl radicals is by far the most extensive for large alkyl radicals. In general their results exhibit the same broad features as those for the metathetical reactions of methyl radicals.

The increase of metathetical reactivity in the series n-heptane, 1-heptene and 1-heptyne illustrates how the rate of abstraction of a constituent hydrogen atom may be determined by structural features.

For the series of alkenes studied by James and Steacie[65], it was found that the activation energy remained constant within experimental error, so that one is tempted to make the conclusion, although there are insufficient results to justify it, that the changes in reactivity of this series are due to changes in the A factor and not in the activation energy. This conclusion was reached from the results of methyl attack on alkenes. On the other hand, with the series of alkanes changes in reactivity towards methyl radicals appear to be due to changes in the activation energy, and not the A factor. No explanation has been put forward to explain these findings. A remarkable feature of Table 1.6. is the similarity of the activation energies of the reactions of n-propyl and s-propyl radicals, for it is generally believed that the strengths of the bonds broken when the radicals are formed from propane differ by three or more k.cal. $mole^{-1}$.

Table 1.7. contains the few results obtained on the hydrogen abstraction reactions of butyl radicals.

TABLE 1.5. THE METATHETICAL REACTIONS OF ETHYL RADICALS

Reactant	Radical Source	E k.cal.mole^{-1}	log A mole^{-1} cm.^{3} sec.$^{-1}$	10^{-6}k at 182°C.	Reference
Deuterium	Diethyl ketone P	13·3	12·3	1	71
Hydrogen	Diethyl ketone P	(11·5)			71
Cyclohexene	Diethyl ketone P	8·2	11·8	72	65
n-Heptane	Diethyl ketone P	10·6	12·0	8	65
1-Heptene	Diethyl ketone P	8·3	11·5	32	65
1-Heptyne	Diethyl ketone P	7·6	11·2	36	65
1-Octene	Diethyl ketone P	8·3	11·5	32	65
Trans-4-octene	Diethyl ketone P	8·7	11·8	42	65
Propionaldehyde	Propionaldehyde P	5·9	11·1	182	(e)
Propionaldehyde	D.T.B.P. + Propionaldehyde T	7·6	11·8	141	72
Methyl ethyl ketone	Methyl ethyl ketone P	8·0	11·3	28	51
Diethyl ketone	Diethyl ketone P	7·8	11·4	45	65,50,~~71~~,73
	Azoethane P	7·6	11·3	44	74
2:2:4:4-Tetradeutero-diethyl ketone	2:2:4:4-Tetradeutero-diethyl ketone P				
$(CH_3\underline{C}D_2)_2\cdot CO$		8·7	11·9	51	63
$(\underline{C}H_3CD_2)_2\cdot CO$		11·7	11·7	4	63
Perdeuterodiethyl ketone	Perdeuterodiethyl ketone P	9·6	11·6	10	75
Azoethane	Azoethane P	7·5	11·2	40	76
Diethyl mercury	Diethyl mercury P	6·2	10·6	42	40

These rate factors are based on $k_c = 10^{14\cdot0}$ mole^{-1} cm.^{3} sec.$^{-1}$ for ethyl radical combination.
The atoms underlined are those attacked in the metathesis.
D.T.B.P. = Di-t-butyl peroxide.
T = radicals produced by thermal decomposition.
P = radicals produced by photolysis.

TABLE 1.6. THE METATHETICAL REACTIONS OF PROPYL RADICALS

Reactant	Radical Source	E k.cal.mole^{-1}	log A mole^{-1} cm.^{3} sec.$^{-1}$	10^{-6}k at 182°C.	Reference
n-PROPYL RADICALS					
n-Butyraldehyde	n-Butyraldehyde P				
n-C_3H_7·CHO		6·7	11·3	120	(a)
n-C_3H_7·CHO		10·8	11·3	1	(a)
Di-n-propyl ketone	Di-n-propyl ketone P	6·5	10·7	38	10
s-PROPYL RADICALS					
Hydrogen	Propylene + H	12·5			86
iso-Butyraldehyde	iso-Butyraldehyde P				
iso-C_3H_7·CHO		6·3	11·3	186	(b)
iso-C_3H_7·CHO		9·5	11·2	4	(b)
Di-iso-propyl ketone	Di-iso-propyl ketone P				
$((CH_3)_2CD)_2$·CO		9·3	11·1	4	11
$((CH_3)_2CD)_2$·CO		11·7	11·8	5	11
Azo-iso-propane	Azo-iso-propane P	6·5	10·4	19	21
PERFLUORO n-PROPYL RADICALS					
Hydrogen	Perfluoro-di-n-propyl ketone P	12·3	12·6	5	87
Deuterium	Perfluoro-di-n-propyl ketone P	13·8	12·8	2	87
Methane	Perfluoro-di-n-propyl ketone P	9·5	11·0	3	59
Ethane	Perfluoro-di-n-propyl ketone P	9·2	12·2	60	59

Results based on $k_c = 10^{14·0}$ mole^{-1} cm.^{3} sec.$^{-1}$ for propyl combination.

+ H, radicals produced by mercury photosensitised addition of hydrogen atom to olefin.

TABLE 1.7. THE METATHETICAL REACTIONS OF BUTYL RADICALS

Reactant	Radical Source	E k.cal. mole^{-1}	log A mole^{-1} cm.^{3} sec.$^{-1}$	10^{-6}k at 182°C.	Reference
n-BUTYL RADICALS					
n-Valeraldehyde	n-Valeraldehyde P	5·4	10·9	200	(c)
s-BUTYL RADICALS					
1-Methyl butyraldehyde	1-Methyl butyraldehyde P	4·9	10·7	219	25
iso-BUTYL RADICALS					
Di-iso-butyl ketone	Di-iso-butyl ketone P	7·6	11·4	55	12

Results based on $k_c = 10^{14\cdot0}$ mole^{-1} cm.^{3} sec.$^{-1}$ for butyl combination.

1.5. ADDITION REACTIONS TO MULTIPLE BONDS

Although the addition of alkyl radicals to multiple bonds has long been recognised, very little quantitative information exists on this class of reaction. The reasons for this situation become apparent when one considers a general example of the simplest case, alkyl radical addition to ethylene:

$$R + CH_2 = CH_2 \quad = \quad RCH_2CH_2 .$$

The experimentalist is not only faced with the usual problem of determining the concentration of the attacking radical, but must also find the rate of formation of the radical product if the rate constant for the above reaction is to be obtained. No matter how small the attacking radical, the determination of the rate of formation of the radical product is complex, owing to the diversity of reactions which such a radical may undergo.

The additions of alkyl radicals to double bonds are of particular interest because they are the reverse reactions of radical decompositions. In the section to follow, on radical decompositions, it will be shown how the activation energies for these reactions may be usefully compared with thermal data, and how the A factors are related to the entropy change of the reaction.

In the gas phase two major general methods of approach have been applied to alkyl radical additions: (a) that involving a material balance of the attacking radical, and (b) that involving an analysis of the products of the reactions of the resulting radical. The results obtained by these methods are summarised in Table 1.8.

Methyl Radical Additions. Mandelcorn and Steacie[88] photolysed acetone as a source of methyl radicals in their studies on the addition of methyl radicals to unsaturates. Between 100 and 280°C. the following mechanism accounts for the methyl radicals:-

$$CH_3 \cdot CO \cdot CH_3 \xrightarrow{h\nu} 2CH_3 + CO \qquad (1)$$

$$2CH_3 = C_2H_6 \qquad (2)$$

$$CH_3 + CH_3 \cdot CO \cdot CH_3 = CH_4 + CH_2 \cdot CO \cdot CH_3 \qquad (3)$$

$$CH_3 + CH_2 \cdot CO \cdot CH_3 = C_2H_5 \cdot CO \cdot CH_3 \qquad (4)$$

and experimentally it has been shown that

$$(2R_{C_2H_6} + R_{CH_4} + R_{C_2H_5 \cdot CO \cdot CH_3})/R_{CO} = 1 \cdot 90$$

where R_X = rate of formation of X. When an olefin such as ethylene is present we have the additional reaction

$$CH_3 + C_2H_4 = C_3H_7 \cdot \qquad (5)$$

Since the presence of the olefin will not affect the rate of production of the carbon monoxide, the material balance becomes

$$(2R^*_{C_2H_6} + R^*_{CH_4} + R^*_{C_2H_5 \cdot CO \cdot CH_3} + R'_A)/R^*_{CO} = 1 \cdot 90$$

where R'_A is the rate of formation of the propyl radical and * indicates the presence of the unsaturate. Since everything else in the above expression can be measured, R'_A can be found by subtraction. This treatment ignores the consumption of radicals by reaction (6)

$$CH_3 + C_3H_7 = C_4H_{10} \qquad (6)$$

which will be most important at low temperatures. Therefore R'_A will be greater than the true rate of addition, R_A, and E'_A will be lower than E_A.

Before the development of gas chromatography it was difficult to measure a quantity of methyl ethyl ketone in a large excess of acetone with accuracy. This difficulty was overcome by writing for any given temperature

$$(2R_{C_2H_6} + R_{CH_4})/R_{CO} = (2R^*_{C_2H_6} + R^*_{CH_4} + R''_A)/R^*_{CO}.$$

R''_A will be lower than R'_A; the difference will be greatest at high temperatures; therefore

$$E''_A < E'_A < E_A.$$

Mandelcorn and Steacie[88] also applied a third approach. This involved the assumption that only one molecule of olefin is converted into higher boiling material for each methyl radical which reacts with an olefin molecule. This ignores further polymerisation by product radicals and addition of acetonyl radicals to the unsaturate. Hence measurements of the rate of disappearance of olefin place an upper limit, R'''_A, on R_A.

The agreement between results for R''_A and R'''_A for the addition of methyl radicals to ethylene, propylene and butadiene was reasonably good.

A more recent determination of the rate of methyl radical addition to ethylene has been made by Brinton[55]. The source of methyl radicals was the pyrolysis of di-t-butyl peroxide and analysis of the products of the propyl radical produced was made by low temperature distillation and the mass spectrometer. Brinton hoped that by keeping the concentration of ethylene low, it would be possible to limit the polymerisation of the ethylene to the initial addition of the methyl radical. Significant quantities of n-hexane were, however, found at all ethylene concentrations. This could only be explained by propyl addition to ethylene and subsequent combination of the pentyl with methyl, as well as the combination of two propyl radicals. By calculating the extent of these hexane forming reactions Brinton derived a rate constant for methyl addition to ethylene.

It may be observed from Table 1.8. that the rate constant for methyl addition to ethylene at 142°C. derived from the work of Mandelcorn and Steacie is the same as that obtained by Brinton, although the rate factors put forward by Brinton are to be preferred, since his method was more direct.

Other values of the activation energy for methyl addition to ethylene have been determined from measurements of the temperature coefficient of

polymerisation[89,90,91]. The method of Raal and Danby[90] is analogous to that described in the experimental sections of this thesis, on radical additions to ethylene. Acetaldehyde was photolysed in the presence of ethylene, but instead of analysing the products, Raal and Danby measured the overall pressure change in the system and analysed for unreacted acetaldehyde. It should be noted that the value of 6·8 k.cal. mole^{-1} for the activation energy for methyl addition to ethylene obtained by this method depends on a value of 9·7 k.cal. mole^{-1} for the activation energy of hydrogen abstraction from acetaldehyde by methyl radicals. If the more recently determined [92,93] value of 7·5 k.cal. mole^{-1} is used for this energy, Raal and Danby's value becomes 4·6 k.cal. mole^{-1}. In general, however, since these determinations of the temperature coefficients of polymerisations depend upon the interpretation of the polymerisation kinetics and values selected for the various activation energies of other reactions involved in the mechanism, they are of doubtful significance.

Ethyl Radical Additions. A material balance method similar to that used by Mandelcorn and Steacie[88], has been developed by James and Steacie[94], in a study of ethyl radical additions to unsaturates, using diethyl ketone as a radical source. The mechanism of photolysis of diethyl ketone below 250°C. is given in section 1.4., from which it may be seen that one molecule of carbon monoxide is equivalent to two ethyl radicals and hence to one molecule of either ethane or butane. The material balance is then

$$(R_{C_2H_6} + R_{C_4H_{10}})/R_{CO} = 1$$

which has been confirmed by experiment. In the presence of an olefin, ethyl radicals add across the double bond to form a larger alkyl radical, which either combines with another ethyl radical or forms a stable product in some other way involving an ethyl radical. Hence, for each molecule of ethylene that reacts in the addition process, two ethyl radicals disappear from the system without

the formation of ethane or butane. The material balance becomes

$$(R^{*}_{C_2H_6} + R^{*}_{C_4H_{10}} + R_A)/R^{*}_{CO} = 1$$

where * denotes the presence of unsaturate and R_A is the rate of formation of the radical resulting from ethyl addition to the double bond. R_A is simply found by subtraction, since all the other rates are measured, and a ratio of rate constants obtained in the normal manner.

The results obtained in this way are given in Table 1.8. The effect of structure on the Arrhenius parameters for the addition of ethyl radicals to the three classes of unsaturate, monosubstituted alkyne, mono substituted alkene and disubstituted alkene, was determined. It was found that the activation energies for the three classes of hydrocarbon had distinctly different values. The addition of ethyl radicals to ethylene has been the object of two independent studies. The mercury photosensitised addition of hydrogen atoms to ethylene was the source of ethyl radicals used by Pinder and Le Roy[95]. The values of the Arrhenius parameters derived from this study do not agree very well with those from the work presented in the later part of this thesis, section 7.2. It is interesting to note, however, that the value of the ratio of rate constants at 111°C. obtained by Pinder and Le Roy[95], $\log k_A/k_C^{\frac{1}{2}} = \bar{1}\cdot92$ ($mole^{-\frac{1}{2}}$ $cm.^{\frac{3}{2}}$ $sec.^{-\frac{1}{2}}$), is in reasonable agreement with the value of 0·17 found by the second method.

The values of the Arrhenius parameters for ethyl addition to ethylene found by the photolysis of propionaldehyde in the presence of ethylene[(e)] are close to those that might have been predicted for the unsubstituted double bond from the work of James and Steacie[94], as is shown in the following table:-

	$E_A - E_C$	$\log (A_A/A_C^{\frac{1}{2}})$ $mole^{-\frac{1}{2}}$ $cm.^{\frac{3}{2}}$ $sec.^{-\frac{1}{2}}$
Unsubstituted ethylene	8·6	5·0
Monosubstituted ethylene	6·9	4·1
Disubstituted ethylene	5·7	3·6

However, it seems likely that the parameters obtained from the photolysis of prionaldehyde/ethylene mixtures have been slightly overestimated.

Larger Alkyl Radical Additions. The rates of addition of n-propyl, s-propyl and n-butyl radicals to ethylene have been measured by the photo-initiated chain decomposition of the appropriate aldehyde in the presence of the olefin (see sections 3.2., 4.2., 5.2.). The method is briefly as follows: when n-butyraldehyde, say, is photolysed in the presence of ethylene, some of the n-propyl radicals add to the double bond to form n-pentyl radicals:

$$\underline{n}C_3H_7 + C_2H_4 = C_5H_{11}\cdot$$

Normally, analysis of the products of the reactions of these pentyl radicals would be complicated, but in these systems, the large marjority ($\sim 85\%$) of pentyl radicals abstract a hydrogen atom from the parent aldehyde to form n-pentane:

$$C_5H_{11} + \underline{n}\text{-}C_3H_7\cdot CHO = C_5H_{12} + C_3H_7\cdot CO.$$

This is due to the high metathetical reactivity of the aldehydic hydrogen. Some of the pentyl radicals ($\sim 10\%$), however, add a further molecule of ethylene to form n-heptyl, which ultimately forms n-heptane. A proportional correction is made to allow for the 1% of the initial radicals which ultimately form nonane. The remaining pentyl radicals dimerise, combine with propyl and disproportionate. The quantities of these products are small and may be estimated on the assumption that n-pentyl radicals react like n-propyl. Hence by analysing for n-heptane and n-pentane and making the necessary corrections, the rate of formation of the pentyl radicals may be obtained. Further, by analysing for the propyl dimer, n-hexane, the usual ratio of rate constants is derived.

The methods applied in the experimental sections of this thesis for ethyl, s-propyl and n-butyl additions to ethylene are analogous to that

described above for n-propyl.

Addition Reactions in the Liquid Phase. A considerable volume of work has been carried out on the addition reactions of alkyl and similar radicals to double bonds in solution. Szwarc has developed a material balance method for this purpose, involving as a source of methyl radicals the decomposition of acetyl peroxide in iso-octane solution. The gaseous products are methane, ethane and carbon dioxide. Two molecules of carbon dioxide are formed from each molecule of the peroxide that decomposes; the ethane is produced by the cage recombination of methyl radicals; and the methane comes from the abstraction, by methyl, of a hydrogen atom from iso-octane:

$$CH_3 + C_8H_{18} = CH_4 + C_8H_{17}. \qquad (7)$$

If an olefin is dissolved in the iso-octane the yield of methane is reduced by reaction (8)

$$CH_3 + U = CH_3U. \qquad (8)$$

It can be shown that

$$k_8/k_7 = \frac{\left(R_{CH_4}/R_{CO_2}\right)_X - \left(R_{CH_4}/R_{CO_2}\right)_Y}{\left(R_{CH_4}/R_{CO_2}\right)_Y} \cdot \frac{[C_8H_{18}]}{[U]}$$

where the subscripts X and Y denote the absence and presence respectively of the unsaturate.

Some of the results obtained by this method are listed in Table 1.9. (after Trotman-Dickenson[96]) and taken in conjunction with the available gas-phase results, they lead to interesting general conclusions. The rate constants in Table 1.9. have been calculated on the basis that the rate constant for the addition to the monosubstituted ethylene is unity.

It is clearly seen from the table that in each series the 1:2-disubstituted ethylene is less reactive than the monosubstituted, although the

effect of substitution is generally to increase the reactivity (see 1:1-disubstituted compounds). This effect is attributed to steric hindrance and is further observed by the greatly reduced reactivity of the tri and tetra substituted compounds.

In general trans-disubstituted ethylenes are more reactive than the corresponding cis compound.

The Relative Rates of Abstraction and Addition of Alkyl Radicals.

The rates of addition (k_a) of ethyl, n-propyl, s-propyl and n-butyl radicals to ethylene have been measured in the experimental sections of this thesis and the rate of addition of methyl to ethylene has been measured by Brinton[55]. Since the rate of reaction of methyl radicals with the sources of the different radicals does not vary with the structure of the alkyl group[101], the rate constant for the reaction of an alkyl radical with its parent aldehyde (k_b) may be regarded as a measure of its activity in transfer reactions. A series of ratios (k_a/k_b) may then be compiled which corresponds to the relative activities of the radicals in addition and transfer. This has been done in the table below for the rate constants at 143°C. which is a convenient temperature near the centre of the experimental ranges. These ratios can be compared with those obtained by Smid and Szwarc[97] for the relative rates at which the radicals abstract from iso-octane (k'_b) and add to benzene (k'_a) at 65°C. (35°C. for s-propyl).

Radical	Me	Et	n-Pr	s-Pr	n-Bu
k_a/k_b	0·45	0·33	0·50	0·63	0·16
	1	0·72	1·1	1·4	0·35
k'_a/k'_b	0·29	2·9	2·0	6·0	-
	1	10	6·9	20	

The second and fourth lines are the ratios divided by the ratio for methyl radicals.

The absence of any correlation between the two sets of results is marked. It is unlikely that it can be solely ascribed to the change from the gas phase to solution. The work in solution did not yield absolute rate constants so it cannot be determined whether the ratios vary because of changes in k'_a or k'_b or both. Probably k'_a/k'_b increases in going from methyl to s-propyl partially because k'_b decreases. k_b does not greatly vary, either because the reactions with the aldehydes are more exothermic than those with iso-octane, or because the polar nature of the aldehydes is important. Further measurements of the rate constants of the higher radicals would be very interesting.

TABLE 1.8. ADDITION OF ALKYL RADICALS TO MULTIPLE BONDS

Reactant	Radical Source	E k.cal.mole^{-1}	log A mole^{-1} cm.^{3} sec.$^{-1}$	$10^{-6}k$ at 142°C.	Reference
METHYL RADICALS					
Ethylene	Acetone P	7·0	11·2	33	88
	D.T.B.P. - T	8·7	12·1	33	55
Propylene	Acetone P	6·0	10·8	44	88
Butadiene	Acetone P	2·5	9·7	240	88
ETHYL RADICALS					
Ethylene	Ethylene + H	5·5	10·0	13	95
	Propionaldehyde P	8·6	12·1	38	(e)
1-Hexene	Diethyl ketone P	6·8	10·9	21	94
1-Heptene	Diethyl ketone P	7·0	11·1	26	94
2:3:3-Trimethyl 1-butene	Diethyl ketone P	5·6	10·2	18	94
1-Octene	Diethyl ketone P	6·7	10·9	23	94
2:4:4-Trimethyl 1-pentene	Diethyl ketone P	5·7	10·6	40	94
1-Heptyne	Diethyl ketone P	8·8	11·9	18	94
n-PROPYL RADICALS					
Ethylene	n-Butyraldehyde P	6·5	10·9	30	(a)
s-PROPYL RADICALS					
Ethylene	iso-Butyraldehyde P	6·9	11·4	59	(b)
n-BUTYL RADICALS					
Ethylene	n-Valeraldehyde P	7·3	11·1	18	(c)

Results for methyl radicals are based on $k_C = 10^{13\cdot3}$ mole^{-1} cm.^{3} sec.$^{-1}$ for methyl combination.

All other results on $k_C = 10^{14\cdot0}$ mole^{-1} cm.^{3} sec.$^{-1}$

TABLE 1.9. RELATIVE REACTIVITIES OF SUBSTITUTED DOUBLE BONDS

GROUP	Methyl (65°C.)				Ethyl (65°C.)	
$=$	ethylene	1·2	ethylene	0·05	-	-
$-=$	propylene	1·0	styrene	1·0	1-heptene	1·0
$\rangle=$	iso-butene	1·6	1:1-diphenyl ethylene	2·0	methyl neo-pentyl ethylene	2·3
			2-phenyl propylene	1·2	methyl t-butyl ethylene	1·1
$\backslash=/$	cis-2-butene	0·12	cis-stilbene	0·04	cyclo-hexene	0·2
$/=\backslash$	trans-2-butene	0·24	trans-stilbene	0·13	trans-di-propyl ethylene	0·2
$\rangle=/$	-	-	triphenyl ethylene	0·06	-	-
$\rangle=\langle$	-	-	tetraphenyl ethylene	0·01	-	-
reference	80		99,100		94	

1.6. DECOMPOSITION REACTIONS.

In general alkyl radicals are known to decompose by three reactions:

$$R = H + r \quad .. \qquad .. (a)$$
$$R = CH_3 + r' \quad .. \qquad .. (b)$$
$$R = C_2H_5 + r'' \quad .. \qquad .. (c)$$

In all cases r is an olefin molecule. This series of reactions could, of course, be extended by decomposition to give a propyl radical and an olefin, but this would require that R be at least a pentyl radical, and very little is known of the decomposition of radicals larger than butyl.

The activation energies for these decompositions are comparatively high; about 40-45 k.cal.mole^{-1} for reaction (a), and about 20-30 k.cal.mole^{-1} for reactions (b) and (c). The difference corresponds to the difference between the strengths of the C - H and C - C bonds.

Alkyl radical decompositions are not easy to measure. Thermally equilibrated radicals only start to decompose at a measurable rate above 200°C., at which temperature the larger radicals may undergo a variety of reactions. Complications due to side reactions are also frequently encountered. Until recently practically all the information which existed on these decompositions was obtained by Bywater and Steacie[14] from the mercury photosensitised decomposition of paraffins. They produced radicals from ethane, propane, n-butane and iso-butane at temperatures from 30 to 500°C.

At room temperature the excited mercury atoms react with alkane molecules

$$Hg^{*} + RH = Hg + R + H \qquad (1)$$

to produce a hydrogen atom and an alkyl radical. The hydrogen atoms may combine in a three body collision or form hydrogen molecules by attack on a molecule of alkane:

$$H + H + M = H_2 + M \qquad (2)$$

$$H + RH = H_2 + R. \qquad (3)$$

The alkyl radicals react mutually in a combination or disproportionation:

$$\left.\begin{aligned} R + R &= R_2 \\ R + R &= RH + r. \end{aligned}\right\} \qquad (4)$$

As the temperature is increased so is the proportion of hydrogen atoms which react with alkane, until the quantum yield for hydrogen production approaches the theoretical maximum of unity.

It is important in this experiment that the percentage conversion of the alkane be small, since both hydrogen and alkenes have much larger quenching cross-sections.

At a sufficiently high temperature decomposition of the alkyl radical begins:

$$R = R' + r \qquad (5)$$

where R' is a hydrogen atom or an alkyl radical which reacts with a molecule of alkane to regenerate an alkyl radical by the chain carrying reaction (6):

$$R' + RH = R'H + R. \qquad (6)$$

According to the above reaction scheme, the number of radicals removed by reaction (4) is equal to twice the number of hydrogen molecules formed at low temperatures. This equality holds until the chain decomposition of the radicals becomes important. Furthermore, since at all temperatures the only chain ending reactions are those involving the interaction of two radicals, the number of radicals reacting by (4) is equal to twice the 'non-chain' hydrogen. This 'non-chain' hydrogen is measured directly at low temperatures and estimated by extrapolation at higher temperatures.

The number of radicals which decompose by reaction (5) is equal to the number of molecules of $R'H$ formed. If $R'H$ is methane or ethane, its rate of formation may be measured directly. If $R'H$ is hydrogen, its rate of formation

is equal to the measured rate of formation of hydrogen minus the rate of formation of 'non-chain' hydrogen. Hence

R_{R_2} = Rate of formation of 'non-chain' hydrogen

$R_{R'H}$ = Rate of formation of R'H

= Total rate of formation of hydrogen - rate of formation of 'non-chain' hydrogen, and if the light intensity is constant,

$$R_{R_2} = k_4[R]^2$$

and $$R_{R'H} = k_5[R]$$

therefore $$k_5/k_4^{\frac{1}{2}} = R_{R'H}/R_{R_2}^{\frac{1}{2}}.$$

The rate constant for decomposition is thus obtained in terms of the rate constant for formation of the dimer. In keeping with the rest of this survey of alkyl radical reactions, the conventional rate constant for alkyl radical combination has been selected as

$$k_C = 10^{14\cdot0} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

The mercury photosensitised decomposition of alkanes, as a method of generating alkyl radicals, suffers from inherent disadvantages. There is always doubt concerning the effective reaction volume. If the concentration of mercury atoms in the reaction vessel is that corresponding to the saturated vapour pressure of mercury at room temperature, 95% of the mercury resonance radiation will be absorbed in the first 3 mm. of the cell. Diffusion will tend to disperse the radicals but it is reasonable to assume, as is done by Trotman-Dickenson,[15] that the reaction zone extends 2·5 cm. from the window into which the light shines. In most cases, since more than one radical species is produced by the decomposition of the alkane, Arrhenius parameters for decomposition cannot be assigned with certainty to a single reaction.

The only other general method so far reported for studying alkyl radical

decompositions, is that of the photoinitiated chain decomposition of aldehydes first used by Gruver and Calvert[25] and extended in the experimental part of this thesis. This method is more direct than the Bywater-Steacie studies of mercury photosensitised decompositions, since in most cases both the products of the radical decompositions are measured directly (this is not the case for reactions of type (a), where only the rate of formation of the olefin can be measured accurately). The concentration of the alkyl radicals in the system is measured in the conventional manner by the rate of formation of the dimer. Hence, as before, a ratio of rate constants is obtained, from which Arrhenius parameters for decomposition are derived. Often corrections have to be applied to allow for the rate of formation of products in the primary photolytic act, which are the same as those from decomposition of the radicals. These corrections are seldom large.

The photolysis of the corresponding ketones has yielded information on the decompositions of n-propyl and s-propyl radicals. The methods of obtaining the results are analogous to that described above for aldehyde photolysis.

Information on the decomposition of n-propyl has also been obtained by Durham, Martin and Sutton[102]. Propyl bromide was reacted with sodium in a flow system and on emerging from a tube at known temperature, the radical reactions were quenched by injection of radioactive iodine into the gas stream. The products were analysed by radio-chemical techniques for propyl iodide and methyl iodide and the proportion of radicals decomposing in a given time at a known temperature was obtained. Hence an activation energy for the decomposition of n-propyl to methyl and ethylene was derived.

Recently Calvert and Sleppy[27] investigated the decomposition of n-propyl by selectively photolysing azomethane in a mixture with n-butyraldehyde. The salient features of their reaction scheme are:

$$(CH_3N)_2 + h\nu = 2CH_3 + N_2$$

$$CH_3 + \underline{n}\text{-}C_3H_7\cdot CHO = CH_4 + C_3H_7\cdot CO$$

$$C_3H_7\cdot CO = C_3H_7 + CO$$

$$C_3H_7 = CH_3 + C_2H_4 \qquad (7)$$

$$C_3H_7 + CH_3 = C_4H_{10} \qquad (8)$$

$$CH_3 + CH_3 = C_2H_6. \qquad (9)$$

Under the conditions of the experiments, there was considerable combination of propyl and methyl radicals. The products were analysed for ethylene, ethane and n-butane.

From the above scheme we have

$$R_{C_2H_4} = k_7 [C_3H_7]$$

$$R_{C_4H_{10}} = k_8 [C_3H_7][CH_3]$$

$$R_{C_2H_6} = k_9 [CH_3]^2$$

from which it may be calculated that

$$k_7 \cdot k_9^{\frac{1}{2}}/k_8 = R_{C_2H_4} R_{C_2H_6}^{\frac{1}{2}}/R_{C_4H_{10}}.$$

In effect, the propyl radical concentration is measured by the rate of formation of the n-butane and ethane, and by making reasonable assumptions concerning k_8 and k_9, Arrhenius parameters may be obtained for reaction (7).

The results obtained by the methods outlined above are summarised in Table 1.10. which is an extension of that drawn up by Trotman-Dickenson[15]. These results are discussed below.

Ethyl Radicals. Ethyl radicals are known to undergo decompositions of type (a) only:

$$C_2H_5 = C_2H_4 + H. \qquad (10)$$

The activation energies of the forward and reverse reactions are related to the

heat of the reaction as follows:

$$\Delta H(10) = E_{10} - E_{-10}.$$

Further, $\Delta H(10) = \Delta H_f^\circ(H) + \Delta H_f^\circ(C_2H_4) - \Delta H_f^\circ(C_2H_5)$

but $\Delta H_f^\circ(C_2H_5) = \Delta H_f^\circ(C_2H_6) + D(C_2H_5 - H) - \Delta H_f^\circ(H)$

$\therefore \Delta H(10) = \Delta H_f^\circ(H) + \Delta H_f^\circ(C_2H_4) - \Delta H_f^\circ(C_2H_6) - D(C_2H_5 - H) + \Delta H_f^\circ(H).$

The values of ΔH obtained in this way are shown in column 2 of Table 1.10. based on the values of D(C - H) shown in column 1. Hence for ethyl decomposition

$$\Delta H(10) = 39 \text{ k.cal.mole}^{-1}$$

from thermal data and

$$E_{10} - E_{-10} = 39{\cdot}5 - 6 \simeq 34 \text{ k.cal.mole}^{-1}$$

from kinetic data, using the value of E_{10} obtained by Bywater and Steacie[14] and $E_{-10} \simeq 6$ k.cal.mole^{-1}, (see note (i), Table 1.10.). The agreement is reasonable, so that E_{10} obtained from aldehyde photolysis[(e)] is seriously in error. Reasons for this discrepancy are discussed in section 7.2.

n-Propyl Radicals. The decompositions of n-propyl by reactions (11) and (12) have been studied by several methods.

$$C_3H_7 = H + C_3H_6 \qquad (11)$$

$$C_3H_7 = CH_3 + C_2H_4 \qquad (12)$$

From Table 1.10. it may be seen that widely differing values of E_{12} have been reported. It is difficult to assess the accuracy of the results of Durham, Martin and Sutton[102] (E_{12} = 19 k.cal.mole^{-1}) since this result was given as a preliminary value, and no further work appears to have been reported. The result obtained by Masson[10] on the decomposition of n-propyl, from di-n-propyl ketone photolysis, is also difficult to assess, since rate constants cannot be obtained from the information given. The estimate of E_{12} = 20 k.cal.mole^{-1} made by Bywater and Steacie[14] may be unreliable, for reasons previously given. It is difficult to see why the results obtained by Calvert and Sleppy[27] disagree

so widely with those obtained in the experimental section of this thesis[a].

The following relations govern the energetics of the decomposition of n-propyl to methyl and ethylene (12).

$$D(CH_3 - CH_2CH_2 -) = \Delta H_f^\circ(CH_3) + \Delta H_f^\circ(C_2H_4) - \Delta H_f^\circ(C_3H_7)$$
$$= E_{12} - E_{-12}$$

but
$$\Delta H_f^\circ(C_3H_7) = \Delta H_f^\circ(C_3H_8) + D(C_3H_7 - H) - \Delta H_f^\circ(H)$$
$$\therefore E_{12} - E_{-12} = \Delta H_f^\circ(CH_3) + \Delta H_f^\circ(C_2H_4) - \Delta H_f^\circ(C_3H_8) - D(C_3H_7 - H) + \Delta H_f^\circ(H).$$

Substituting and using the value of E_{12} obtained by photoinitiated chain decomposition of n-butyraldehyde[a] and E_{-12} by Brinton[55], we have

$$D(C_3H_7 - H) \simeq 105{\cdot}6 \text{ k.cal.mole}^{-1}.$$

A similar calculation may be carried out for the decomposition of n-propyl into propylene and a hydrogen atom. From this it may be shown that

$$D(C_3H_7 - H) \simeq 104{\cdot}1 \text{ k.cal.mole}^{-1},$$

if the E_{-11} is 5 k.cal.mole^{-1}. Although the two determinations are in as good agreement as could be expected, little reliance should be placed on the second determination because the activation energy was not properly determined (see section 3.2.). The calculated dissociation energy is considerably higher than would have been expected. It would be lower if E_{12} had been underestimated or if $\frac{1}{2} E_c$ (n-propyl combination) is greater than zero. It does not seem likely that either value can be sufficiently in error to reduce $D(C_3H_7 - H)$ from equality with $D(CH_3 - H)$ to equality with $D(C_2H_5 - H)$ or about 98 k.cal.mole^{-1}. The high value for $D(C_3H_7 - H)$ which has been reported on the basis of totally different determinations[103,104] is strongly supported by the results from photoinitiated chain decomposition of n-butyraldehyde.

The value of $E_{12} \simeq 35$ k.cal.mole^{-1} obtained by Calvert and Sleppy[27], in contrast to the above results, favours a much lower value for $D(C_3H_7 - H)$. The situation is not satisfactory.

s-Propyl Radicals. The agreement between different determinations of Arrhenius parameters for the decompositions of s-propyl is much better than for n-propyl. For the decomposition

$$\text{s-}C_3H_7 = H + C_3H_6 \qquad (13)$$

the agreement between the work of Heller and Gordon[11] and that from the experimental sections of this thesis[(b)] is excellent. On the other hand, their values of E_{14} and A_{14} are to be preferred,

$$\text{s-}C_3H_7 = CH_3 + C_2H_4 \qquad (14)$$

since their rates of formation of methane and ethylene balanced, whereas in the photolysis of iso-butyraldehyde they did not (see section 4.2.).

Hence using the best values of E_{13} and E_{14} it may be shown by a calculation similar to that carried out for n-propyl radicals, that

$$D(\text{s-}C_3H_7 - H) = E_{-13} + 96{\cdot}8 \text{ and } E_{-14} + 89{\cdot}3.$$

The incomplete evidence presently available indicates that the activation energies for the addition of hydrogen atoms and methyl radicals do not differ by more than 1 or 2 k.cal.mole^{-1}. Hence, there is a discrepancy between the determinations of E_{13} and E_{14} of about 7 k.cal.mole^{-1}.

The value of $D(\text{s-}C_3H_7 - H)$ that is currently accepted as the most probable is 94 k.cal.mole^{-1}. If E_{-14} is allotted the reasonable value of 8 k. cal.mole^{-1} we have $D(\text{s-}C_3H_7 - H) = 89{\cdot}3 + 8 = 97$ k.cal.mole^{-1} from the kinetic measurements. This value is, within the limits of the accumulated experimental errors, equal to that which is accepted. The agreement would be even more striking if the combination of s-propyl radicals has a small positive activation energy (E_C). For $D(\text{s-}C_3H_7 - H) = 97 - \frac{1}{2} E_C$.

The result for $D(\text{s-}C_3H_7 - H)$ obtained above may be of little significance. Before the work of Heller and Gordon[11] was published and the work on iso-butyraldehyde photolysis[(b)] was started, it was thought that reaction (14) would

not occur, since information in the literature indicated that the parallel reactions of s-butyl are very slow.[106] Furthermore, even although this reaction (14) is now known to occur, it is not established whether the overall decomposition occurs in one step in which the isomerisation and decomposition are simultaneous. Isomerisation may occur first and it may be the rate of this process that is measured. The isomerisation is exothermic and yields n-propyl containing energy considerably in excess of the critical energy for decomposition. Unless it is deactivated by collision it will necessarily decompose. At the comparatively low pressures of the experiments few of the radicals are likely to be deactivated.

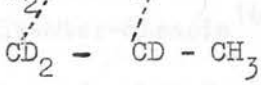
An indication that the isomerisation occurs first with a high activation energy may be seen in the work of Brinton[55] on the addition of methyl to ethylene. If decomposition and isomerisation of large radicals were simultaneous processes, the addition of small radicals to olefins and the isomerisation of the resultant radical would also be simultaneous. Hence the addition of methyl to ethylene could yield s-propyl as well as n-propyl. Brinton found n-butane (from n-propyl + methyl) in his products but no iso-butane. There is therefore no evidence for isomerisation in this case. Only if the decomposition and isomerisation are simultaneous can the energetics of the processes be calculated.

n-Butyl Radicals. The comparatively large rate constant of reaction (15)

$$\text{n-}C_4H_9 = CH_3 + C_3H_6 \qquad (15)$$

found in the photoinitiated chain decomposition of n-valeraldehyde[(c)] is surprising because it was previously supposed that n-butyl did not yield methyl and propylene. The work of Frey and Hepp[105] on the pyrolysis of di-n-butyl mercury seemed fairly conclusive. No satisfactory explanation can be given

for the absence of propylene in their products. McNesby, Drew and Gorden[106] studied the products of the decomposition of butyl radicals formed by the reactions of methyl radicals with $CH_3CD_2CD_2CH_3$. They found that the propylene formed always contained three deuterium atoms. They supposed that this could only come from the decomposition of $CH_3CD\ CD_2 - CH_3$ and that $CH_2CD_2CD_2CH_3$ could only yield $CH_2CD\ CD_3$ and CH_3 by the transfer of a D atom between adjacent carbons. It is, however, possible that a four centre activated complex may be involved in the transfer of the D atom as shown



which would yield CH_2D and $CD_2CD\ CH_3$. At the time McNesby, Drew and Gordon wrote no certain example of alkyl isomerisation was known. But as we have already seen, s-propyl will decompose to methyl and ethylene. The question of simultaneous decomposition and isomerisation arises again and it would appear that experiments on the reverse addition of methyl to propylene would be profitable.

A treatment of the energetics of reaction (15) gives a value of $D(\underline{n}\text{-}C_4H_9 - H)$ of $E_{-15} + 92{\cdot}5$ or a value for the C - H bond strength of about 100 k.cal.mole^{-1} which is reasonable, but for the reasons outlined above, little significance should be attached to this value.

The decomposition of n-butyl according to reaction (16),

$$\underline{n}\text{-}C_4H_9 = C_2H_5 + C_2H_4 \qquad (16)$$

where no isomerisation is involved, should give a value of E_{16} leading to $D(\underline{n}\ C_4H_9 - H)$ directly comparable with that from thermal data. By treatment of reaction (16) as before we get

$$D(\underline{n}\text{-}C_4H_9 - H) = E_{-16} + 98.$$

E_{-16} is about 8 k.cal.mole^{-1} if the combination of ethyl radicals has no activation energy[(e)]. Hence $D(\underline{n}\text{-}C_4H_9 - H) \simeq 106$ k.cal.mole^{-1}. This value

seems improbably high. The most likely cause of the discrepancy is the underestimation of E_{16}. The low value of A_{16} tends to support this supposition.

The rate constants, A factors and activation energies, that can be deduced from the work of Bywater and Steacie[14] on the mercury photosensitised decomposition of n-butane at high temperatures agree well with those derived for n-butyl radicals from photolysis of n-valeraldehyde[(c)]. It is, however, likely that they were dealing largely with s-butyl radicals.

s-Butyl Radicals. Apart from the Bywater-Steacie[14] results the only quantitative information on the decomposition of s-butyl comes from the photolysis of 1-methyl butyraldehyde by Gruver and Calvert.[25] They studied the reaction

$$\text{s-}C_4H_9 = CH_3 + C_3H_6 \qquad (17)$$

and on first publishing their results they put forward the rate constant for reaction (17) of

$$k_{17} = 10^{11.7} \exp.(-24000/RT) \text{ sec.}^{-1}$$

if the rate constant for butyl combination is given by

$$k_c = 10^{14.0} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}.$$

Calvert later[107] revised this to

$$k_{17} = 10^{15.6} \exp.(-30600/RT) \text{ sec.}^{-1}.$$

The usual treatment of the energetics yields

$$D(\text{s-}C_4H_9 - H) = 90 + E_{-17}$$

if $E_{17} = 30.6$ k.cal.mole^{-1}. Hence $D(\text{s-}C_4H_9 - H) \simeq 96$ k.cal.mole^{-1} if E_{-17} = 6 k.cal.mole^{-1} [88], which agrees very well with the presently accepted value. However, the values of E_{17} and A_{17} conflict seriously with those from mercury photosensitisation.

iso-Butyl and t-Butyl Radicals. The mercury photosensitised decomposition of iso-butane provides the only quantitative information available

at present on the decomposition of the above radicals. However, as mentioned previously it is difficult to obtain unambiguous information from this system since inevitably both radicals are present.

It is hoped that the photoinitiated chain decomposition of the corresponding aldehydes will yield reliable results on these decompositions.

Other Alkyl Radicals. It is interesting to note that cyclopropyl and cyclopentyl radicals, produced by reaction of methyl with the corresponding cyclanes[108], isomerise rapidly at 375°C. Allylic radicals are formed by a rupture of C - C bonds and those from cyclopentyl decompose to allyl and ethylene.

Radical Decomposition and A-Factors. The A factor for a radical decomposition (A_f) is related to that of the reverse addition of a smaller radical to an olefin (A_b) and the entropy change of the reaction ΔS as follows:

$$\Delta S = R \ln A_f/A_b .$$

The entropies of the radicals, and hence the overall entropy changes, can be calculated with sufficient accuracy by standard methods. The A factors for the addition of methyl and ethyl radicals in the gas phase are of the order of 10^{11} mole^{-1} cm.^{3} sec.$^{-1}$, as is predicted by transition-state theory. These values lead to A factors of the order of 10^{13} sec.$^{-1}$ for the decomposition of radicals, the normal value for unimolecular decompositions. The overall picture from Table 1.10. shows that alkyl radical decompositions occurring with loss of a hydrogen atom have A factors roughly in agreement with theoretical predictions, but for most other decompositions the A factors experimentally found appear to be decidedly low. On the other hand, the A factors obtained by Calvert et al[25,107] seem improbably high.

Radical Decompositions and Unimolecular Theory. Since alkyl

radical decompositions are unimolecular reactions, they should provide valuable experimental information to check existing theories of unimolecular reactions. One of the main features of unimolecular reaction theory is that the unimolecular rate constant should be dependent upon overall pressure in the system. The fall-off in rate constant with decreasing pressure is well known in this respect. In section 3.2. of this thesis, some preliminary studies were carried out on the effect of pressure on the rate of decomposition of n-propyl radicals. It was shown that by increasing the pressure in the system, either by adding carbon dioxide to the normal pressure of aldehyde, or by starting with aldehyde pressures greater than those normally employed, the rate constant for decomposition to methyl and ethylene was definitely increased, while that for decomposition to a hydrogen atom and propylene was less affected. Reduced pressure in the system produced a reduction in the rate constant for decomposition to methyl and ethylene but had less effect on decomposition to propylene. These investigations were not extended further since the apparatus was not suitable for this type of work. However, they showed that alkyl radical decompositions should be a good source of experimental information on unimolecular reactions.

TABLE 1.10. THE DECOMPOSITION OF ALKYL RADICALS

RADICAL and REACTION	C-H bond	ΔH	E_D (exp.)	log A_D (exp.)	k_D at 400°C.	Ref.	log A_{-D} (calc.)	log A_{-D} (exp.)	E_{-D} (exp.)	Ref.
LOSS OF H ATOM										
C_2H_5	98	39	39·5	14·0'	16	14	13	13·5(i)	4·1(i)	115
			31	11·2	13	(e)				
n-C_3H_7	99	35	38*	14·6*'	200	14	13	14·4*(i)	5·0(i)	115
			35	13·6	159	(a)				
s-C_3H_7	94	40	38*	14·6*'	200	14	13	14·4*(i)	5·0(i)	115
			36·9	13·8	63	(b)				
			35	13·1	50	11				
n-C_4H_9	101	31-33	high*	-	-	14	-	-	-	
s-C_4H_9	94	38-40	high*	-	-	14	-	-	-	
iso-C_4H_9	100	32	40*	15·6*'	400	14	14	-	-	
t-C_4H_9	90	42	40*	15·6*'	400	14	14	-	-	

E_D and A_D refer to the decomposition reaction; E_{-D} and A_{-D} refer to the reverse reaction.

* indicates results from source where it is uncertain which radical decomposes or is formed.

' indicates maximum value of log A_D as calculated by Trotman-Dickenson (109), but corrected for $k_C = 10^{14·0}$ mole^{-1} cm.^{3} sec.$^{-1}$ for radical combinations.

log A_{-D}(calc.) have been calculated from entropy changes[110].

Units; C-H bond, ΔH and E, k.cal.mole^{-1}; A_D, k_D, sec.$^{-1}$; A_{-D}, mole^{-1} cm.^{3} sec.$^{-1}$.

(i) These results are based on the Arrhenius parameters for the reaction H + H_2S = H_2 + HS derived by Darwent and Roberts[116], which in turn depend on the values of the parameters for the reaction D + H_2 = DH + H obtained by Farkas and Farkas[117]. These latter results have been shown to be incorrect[118]. The activation energy for hydrogen addition to olefins is probably nearer 6-7 k.cal. mole^{-1}.

(ii) There is no evidence that the addition of ethyl radicals to ethylene occurs with simultaneous isomerisation of n-butyl to s-butyl. The products of the addition of ethyl to ethylene(e) contained only n-hexane (from n-butyl + ethyl or n-butyl + ethylene) and no 3-methyl pentane.

TABLE 1.10. (continued)

RADICAL and REACTION	C-H bond	ΔH	E_D (exp.)	log A_D (exp.)	$10^{-2}k_D$ at 400°C.	Ref.	log A_{-D} (calc.)	log A_{-D} (exp.)	E_{-D} (exp.)	Ref.
LOSS OF CH_3 RADICAL										
n-C_3H_7	99	23	20*	9·2*'	5	14	6	12·1	8·7	55
			19	-	-	10,102				
			25·2	11·7	32	(a)				
			34·9	15·8	316	27				
s-C_3H_7	94	28	20*	9·2*'	5	14	6	-	-	
			29·5	10·6	0·11	(b)				
			32·5	12·0	0·25	11				
n-C_4H_9	101	18	23*	11·2*'	55	14	8	11·2*	6·0*	88
			27·1	12·1	20	(c)				
s-C_4H_9	94	25	23*	11·2*'	55	14	8	11·2*	6·0*	88
			30·6	15·7	6026	107				
iso-C_4H_9	100	21	18·5*	8·7*'	5	14	5	11·2*	6·0*	88
t-C_4H_9	90	32	18·5*	8·7*'	5	14	5	-	-	
LOSS OF C_2H_5 RADICAL										
n-C_4H_9	101	19	23*	11·2*'	55	14	8	12·1*	8·6*	(e)
			22·0	11·2	120	(c)				
s-C_4H_9	94	26	23*	11·2*'	55	14	8	(ii)	(ii)	

CHAPTER II

GENERAL EXPERIMENTAL.

A description of the apparatus and procedure common to the photolyses of all four aldehydes will be given in this chapter. Any minor deviations will be dealt with in the separate chapters to follow.

2.1. KINETIC AND ANALYTICAL APPARATUS. The apparatus as shown in Fig. 2.1. constituted a static system. The cylindrical quartz reaction vessel (R.V.), volume 177 $cm.^3$, was connected to a conventional vacuum line. Pyrex glass was used throughout the apparatus. The pumping system consisted of a two stage mercury diffusion pump backed by a rotary oil pump, and was capable of reducing the pressure in the apparatus to about 10^{-5} mm. Hg. after about forty minutes pumping.

The reaction vessel was also connected to the analytical section, which consisted of a train of three traps, T_1- acetone dry ice, T_2- liquid oxygen, and T_3- liquid oxygen boiling at reduced pressure, and a three stage mercury diffusion pump (P) situated between T_1 and T_2. Gases passing through these traps were pumped into a gas burette through a non-return mercury float valve (F) by means of a Toepler pump. The Toepler pump - gas burette was also fitted with a McLeod gauge (M). The gas burette was calibrated before being fitted to the apparatus, by weighing mercury filling the various volumes. The sections of the burette as shown in the diagram had the following volumes:-

A	=	0·140 cm.^{3}
A + B	=	0·291 cm.^{3}
A + B + C	=	3·91 cm.^{3}
A + B + C + D	=	23·41 cm.^{3}
A + B + C + D + E	=	153·9 cm.^{3}

The three-way stopcock (S_1) at the top of the gas burette led on one side to the high vacuum line, and on the other to two U tubes and a small tube filled with copper oxide wire. The first of these U tubes (U_1) contained activated silica gel, mesh size 30 to 120. The volume of this section of the apparatus was kept as small as possible by using capillary tubing where appropriate. Gases condensed in the low temperature distillation train were not passed into the gas burette but were distilled through a short absorbent tube (A.T.) packed with 25 - 50 mesh powdered firebrick, on which was suspended 25% by weight of a paste of sodium bisulphite in ethylene glycol.(g) These gases were then either passed directly into the injection system for chromatographic analysis or into a tapped container, and subsequently into the injection system.

The apparatus also contained a storage bulb (S) with trap and blow-off manometer for added gases, and a reservoir (R) for aldehydes. A mercury manometer (M_1) was attached on one side to the reaction vessel, and on the other to the high vacuum line. A low vacuum line was attached at points marked L on the diagram of the apparatus.

The reaction vessel was contained in an electrically heated cylindrical coaxial furnace (F_1). This furnace was constructed of two parts, such that they contacted tightly over the centre of the reaction vessel, and each part was separately wired, although electrical contact was made at the junction. It was found that the two parts of the furnace had to be wired in parallel from a variac to obtain the higher temperatures required, and, further, that to maintain a

temperature gradient of ± 2°C along the length of the reaction vessel (20 cm.) it was necessary to have a shunt of 18 ohms across one half of the furnace. The temperature was maintained to ± 1°C during a run. A thermocouple well extending the entire length of the furnace passed directly under the quartz cell. One end of the furnace contained a quartz window.

The temperature in the reaction vessel was measured by means of a thermocouple constructed from commercial T_1/T_2 wires. The hot junction was placed below the centre of the cell, and the cold junction was maintained at 20°C in a thermos flask containing water. The potential differences were measured on a Tinsley D.C. potentiometer, with a Doran galvanometer. The temperatures were calculated from the T_1/T_2 calibrations supplied by the manufacturers. The reaction cell was illuminated by the unfiltered light from a 125 W. or 250 W. medium pressure mercury arc (X) which was allowed twenty minutes for warming up. An aluminium foil reflector was placed behind the lamp. The intensity of illumination was varied by altering the position of the lamp. It was found that, when the lamp was very close to the window of the furnace, the temperature in the furnace rose slightly. This was offset by blowing a gentle stream of air onto the window.

The copper-oxide tube (C.F.) was housed in a small close-fitting electrically heated furnace (F_2), which was constructed from pyrex glass tubing wound with resistance wire and lagged with several layers of asbestos paper. A thermocouple well was placed along the length of this furnace.

2.2. APPARATUS FOR GAS CHROMATOGRAPHY. A schematic diagram of the chromatographic apparatus is given in Fig. 2.2. The flow of carrier gas, usually hydrogen, from a commercial cylinder was split, passing on the one hand to a series of two or three water bubblers which controlled the pressure head of gas and therefore the rate of flow, and on the other hand through a series of buffering

vessels. These vessels were constructed from small tubes joined up with very fine capillary tubing, and they served to iron-out any irregularities in the rate of flow of the carrier gas. The gas stream was split again into parts (1) and (2). Part (1) passed through the injection system. This consisted of a W tube which could either be by-passed, while being connected to the high vacuum line, or inserted in the flow. On emerging from the injection system part (1) passed into the analysing column. Part (2) passed into an identical balancing column. These columns were constructed from U tubes of pyrex glass (5 mm. I.D.) and were contained in a fibre glass jacket at room temperature. More details of the column packings, etc. will be given in the chapters to follow.

Both parts of the flow then passed into the thermal conductivity cell. This consisted of a solid brass block through which were drilled two identical channels. Stretched above similar parts of each channel were tungsten filaments of resistance approximately 10 ohms.

Finally, on emerging from the conductivity cell the gas streams each passed through one buffering vessel, which increased the stability of the base line in the recorder.

The electrical circuit for the conductivity cell is shown in Fig. 2.3. The voltage for the Wheatstone Bridge circuit was supplied by two 2 volt batteries, and was maintained at 3·90 v. by means of a 2 ohm variable series resistance. The filaments (F) in the thermal conductivity gauges formed two arms of the Wheatstone Bridge, and the other two arms consisted of approximately 100 ohm resistances. The 10,000 ohm rheostat across one of these 100 ohm resistances was used to adjust the balance of the bridge. The off-balance current set up when a gas sample passed through the analysing gauge was fed into a 0·5 m.V. Sunvic recorder via a voltage divider by which a change in sensitivity of approximately five could be effected.

2.3. CHROMATOGRAPHY CALIBRATIONS. Hydrocarbons from C_2 to C_8 were analysed by the gas chromatography system, and for each gas it was necessary to carry out a series of calibrations. The procedure consisted of introducing measured volumes of the gas into the injection system of the apparatus. A small gas burette, which was sealed at one end in order that the gas being measured would have as little contact as possible with stop-cock grease, was constructed for this purpose. The sample was then analysed and a peak obtained on the recorder. In the case of sharp peaks, a calibration graph was constructed by plotting peak height against μ moles of gas for a series of samples, and for broader peaks the area was plotted against μ moles of gas. A calibration curve had to be obtained for each gas under each set of analytical conditions, i.e. different columns and different flow rates.

The sample gases used for calibrations were as follows:-

Ethylene, Ethane, Propane, n-Butane and iso-Butane were obtained directly from commercial cylinders and were $\rangle$ 98% pure.

Propylene was obtained pure by dehydrating iso-propanol with phosphorous pentoxide.

1-Butene and 2-Methyl Propylene (iso-Butene) were obtained by dehydrating the corresponding butanol. Both samples contained other butenes. (See Note 1)

2-Methyl Butane (iso-Pentane) was a commercial sample containing other pentanes. (See Note 1)

n-Pentane, neo-Pentane, 2-Methyl Pentane, 2:3-Dimethyl Butane, n-Heptane and n-Octane (see Note 2) were D.S.I.R. samples and were pure.

n Hexane was a commercial sample containing other hexanes. (See Note 1)

1-Methyl Hexane was assumed to have the same sensitivity as n-Heptane. (See Note 1)

Note 1. In this work it was found that under the same column conditions isomeric hydrocarbons had the same sensitivity, within experimental error (~ 2%), i.e. n-butane and iso-butane, n-pentane and neo-pentane, 2-methyl pentane and 2:3-dimethyl butane, and therefore the samples containing isomers were regarded as one substance for the purposes of calibration.

Note 2. The vapour pressure of n-octane at room temperature is only of the order of 1 cm., and it was therefore not possible to use the calibrating burette in this case. An accurate mixture of n-heptane and n-octane was carefully weighed out in a stoppered weighing bottle, and samples of the mixture analysed. Knowing the n-heptane calibration, and the ratio of n-octane to n-heptane from the weights, it was thus possible to calibrate the n-octane.

2.4. PROCEDURE FOR A RUN. The apparatus was pumped out to a pressure of 10^{-5} mm. Hg. or less. The aldehyde and any gases to be added were completely degassed. A quantity of aldehyde was introduced into the reaction vessel, and its pressure measured on the manometer. Any gases to be added were then introduced, and the pressure reading again taken. The temperature was noted, and the reaction initiated by removing a shutter placed between the lamp and the window of the furnace. A stop-watch was simultaneously started. The reaction was terminated by switching off the lamp and, at the same time, the watch was stopped. With runs at the higher temperatures, where thermal reaction might occur, the products and unreacted aldehyde were immediately pumped out of the reaction vessel into the low temperature distillation system. Ten minutes pumping with the Toepler pump was usually sufficient to collect the non-condensable gases into the gas burette. When this separation was complete, as indicated on

the McLeod gauge, the total amount of non-condensable gases was measured in the gas burette. The non-condensable fraction always contained hydrogen, methane, and carbon monoxide, and was passed into the U tube containing silica gel cooled in liquid oxygen. The uncondensed hydrogen was brought back, measured, and pumped off. A correction was applied to allow for the sharing ratio between the gas burette and U tube/copper oxide furnace system. The silica gel was heated in hot water, the carbon monoxide oxidised in the copper oxide furnace at 320°C (see Note 3) as it came off, and the carbon dioxide condensed in U_2 with liquid oxygen. The methane was then measured, and the carbon monoxide calculated by difference.

Note 3. The oxidation of carbon monoxide usually took one hour or even longer. Many attempts were made to speed up this process, by using pre-activated copper oxide wire, granular micro-analytical copper oxide, etc., but none were entirely successful.

The condensable fraction was passed through the short absorbent column (A.F.) to remove the aldehyde.[g] If ethylene had been added to the reaction mixture it was similarly removed by a column of firebrick mixed with mercuric acetate/mercuric nitrate/ethylene glycol,[g] or if carbon dioxide had been added it was removed by a column of soda lite. The gases that were not absorbed were then passed, either directly or via a tapped vessel, into the injection system of the chromatographic unit and analysed.

2.5. SPECIMEN RUN (Photolysis of Propionaldehyde)

Run No.184.

Furnace temperature = 427°A.
Room temperature = 293°A.
Propionaldehyde pressure = 72·8 mm.
Initial [Propionaldehyde] = $2{\cdot}74 \times 10^{-6}$ mole cm.$^{-3}$.
Length of Run = 1020 seconds.

Analysis of non-condensable gases - gas burette

Product	Time of oxidation (hours)	Gas burette reading	Volume of burette	Pressure of gas in burette (cm.)	μ Moles of product	μ Moles of product corrected*	Rate of formation of product 10^{12} mole cm.$^{-3}$ sec.$^{-1}$
$H_2 + CO + CH_4$	-	33·62	A + B + C	11·96	25·6	-	-
H_2	-	29·57	A + B	3·91	0·623	0·685	3·80
CH_4	½	34·50	A + B	-	-	-	-
CH_4	1	29·37	A + B	-	-	-	-
CH_4	1½	29·37	A + B	3·71	0·591	0·650	3·60
CO	-	-	-	-	-	24·2	135

* This correction is for the sharing ratio between gas burette/U tube, CuO furnace.

Analysis of condensable gases - gas chromatography

Product	Peak area or height on chromatogram	μ Moles of product	Rate of formation of product-10^{12} mole cm.$^{-3}$ sec.$^{-1}$
Ethylene	0·10 sq.in.	0·40	2·22
Ethane	6·35 in.	17·7	98·1
Butane	0·53 sq.in.	2·69	14·9

Calculation of mean [Propionaldehyde]

Time of run	R_{CO} 10^{12} mole cm.$^{-3}$ sec.$^{-1}$	[CO] μ mole cm.$^{-3}$	initial [ALD.] μ mole cm.$^{-3}$	final [ALD.] μ mole cm.$^{-3}$	mean [ALD.] μ mole cm.$^{-3}$	% Decomp.
1020 secs.	135	0·138	2·74	2·60	2·67	5·0

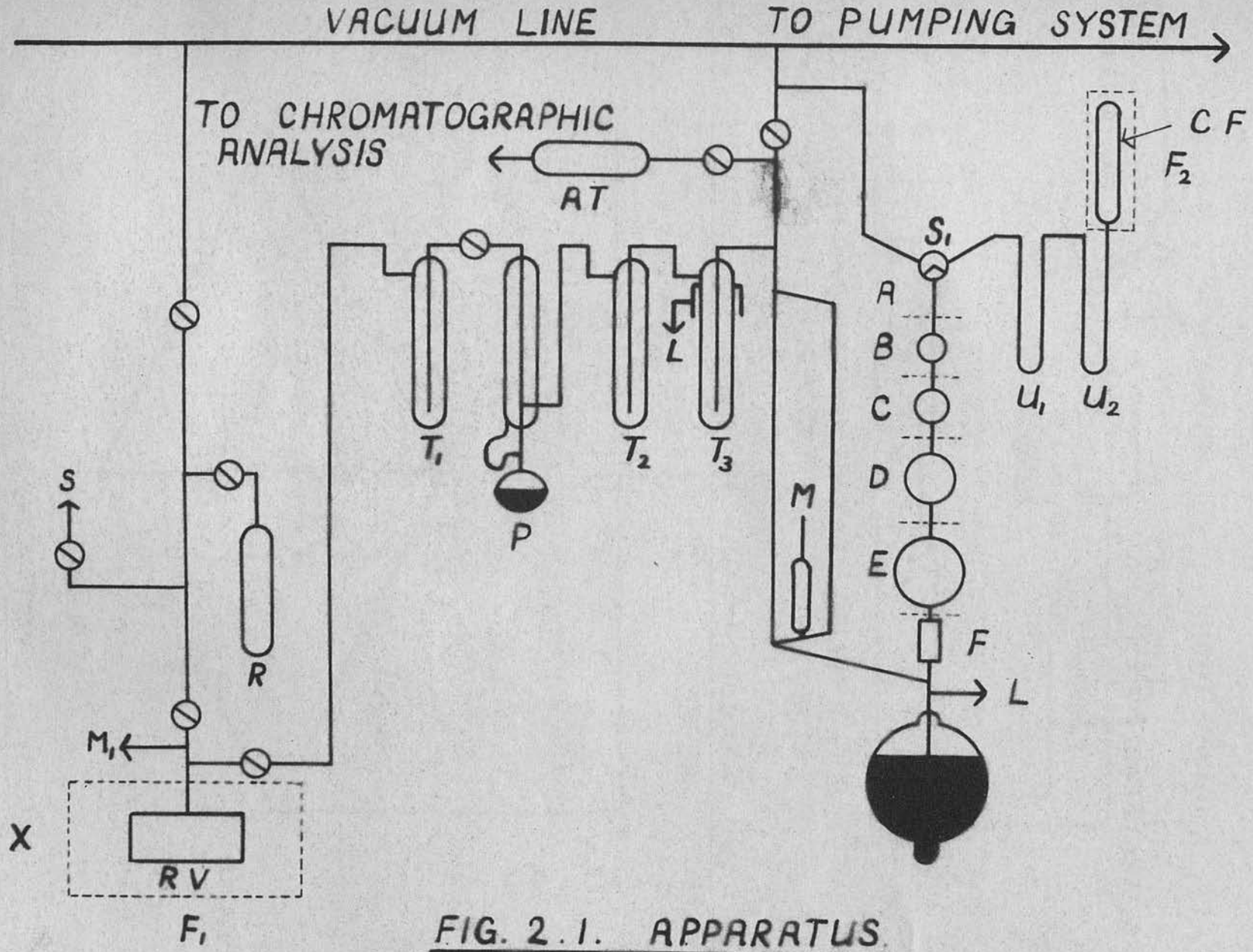


FIG. 2.1. APPARATUS.

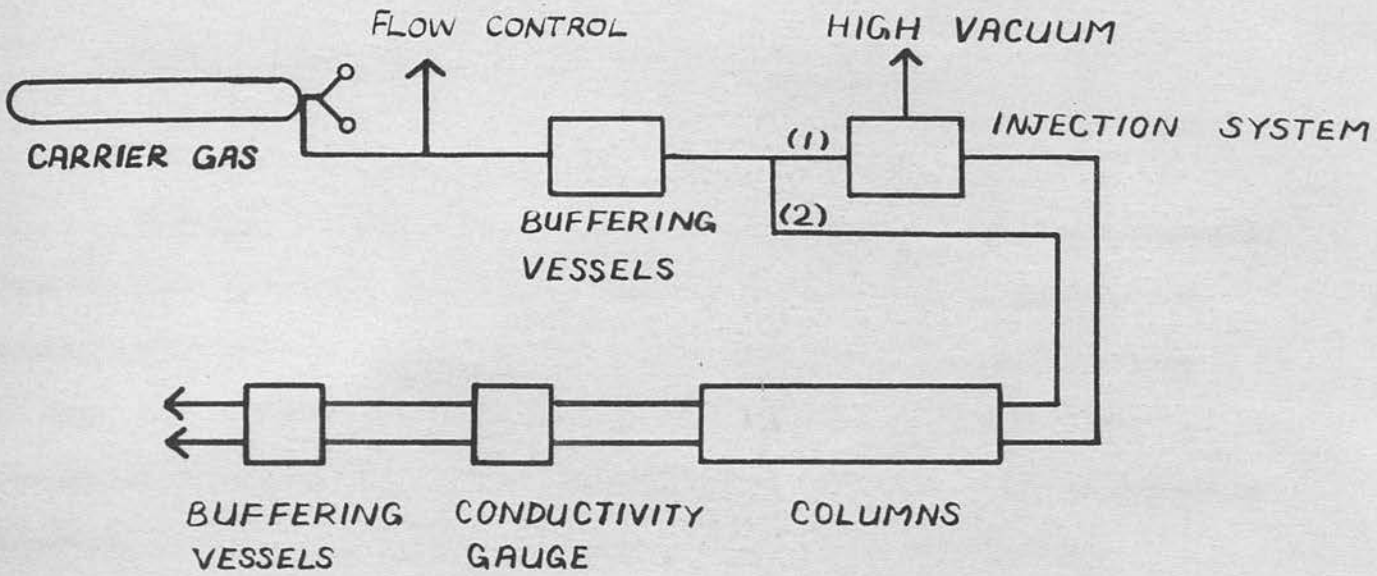


FIG. 2.2 SCHEMATIC DIAGRAM OF CHROMATOGRAPHY UNIT

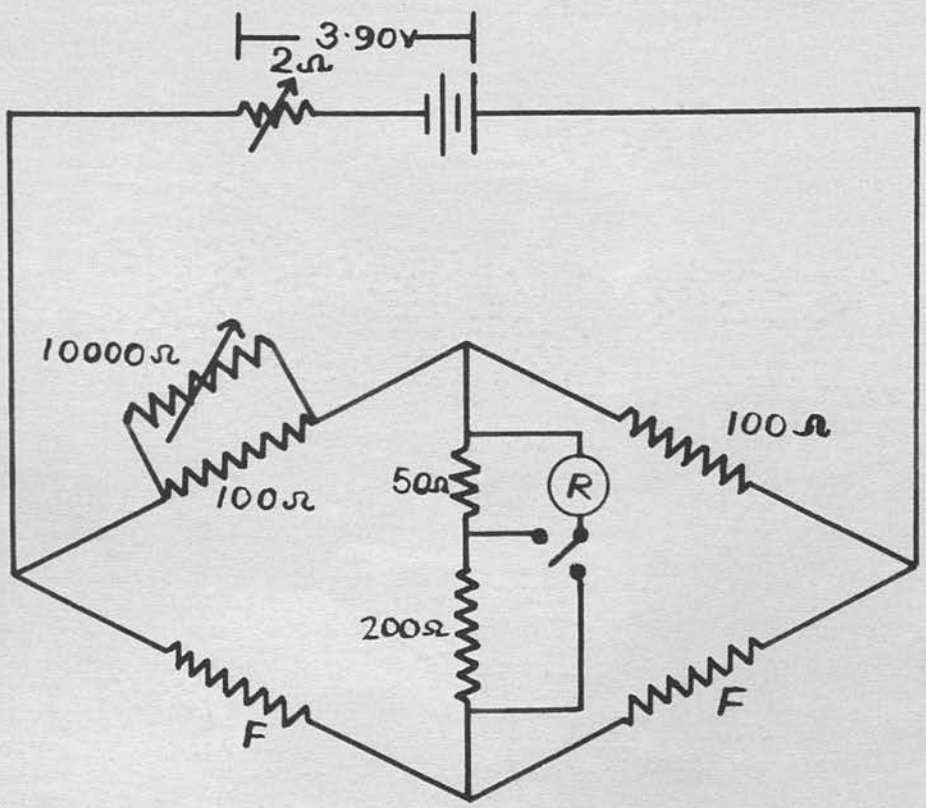


FIG. 2.3 CIRCUIT FOR CONDUCTIVITY GAUGE

CHAPTER III

n-PROPYL RADICALS FROM THE PHOTOLYSIS OF n-BUTYRALDEHYDE

Summary. The photoinitiated chain decomposition of n-butyraldehyde, alone and when mixed with ethylene or propionaldehyde, has been studied. A mechanism that accounts for the rates of formation of the principal products has been constructed. On the assumption that the rate constant for the combination of n-propyl radicals is given by log k = 14, the following Arrhenius parameters of the principal rate-determining reactions have been found:

		log A	E
$2C_3H_7$	= $C_3H_6 + C_3H_8$	13·20	0
$C_3H_7 + C_3H_7\cdot CHO$	= $C_3H_8 + C_3H_7\cdot CO$	11·3	6·7
$C_3H_7 + C_3H_7\cdot CHO$	= $C_3H_8 + C_3H_6\cdot CHO$	11·3	10·8
C_3H_7	= $CH_3 + C_2H_4$	11·7	25·2
C_3H_7	= $H + C_3H_6$	13·6	35·0
$C_3H_7 + C_2H_4$	= C_5H_{11}	10·9	6·5

where k and A are in units of mole^{-1} cm.^{3} sec.$^{-1}$ or sec.$^{-1}$, and E is in k.cal. mole^{-1}. The rate constant for the combination of ethyl and propyl is twice the geometric mean of the constants for the autocombinations.

3.1. EXPERIMENTAL.

Materials. B. D. H. n-butyraldehyde was dried (Ca SO_4) and fractionated. A constant boiling fraction was distilled under vacuum and degassed. B. D. H. propionaldehyde was purified by bulb to bulb distillation with rejection of head and tail fractions. Ethylene was obtained from B. O. G. cylinders and carbon dioxide was I.C.I. Drikold.

Apparatus. This was essentially as described in Chapter II with the additions below. The 125 W. lamp was used throughout the study. The chromatographic system contained two types of column. Column A (length 300 cm.) was packed with 25-52 mesh firebrick + 20% dibutyl phthalate. Column B (length 150 cm.) was packed with activated alumina impregnated with ½% squalane. A tap system was arranged so that after the lower boiling materials through propylene had cleared columns A and B, the hexane could be taken directly from column A. The flow rate was about 30 $cm.^3$/minute and for runs 1 to 13 the carrier gas was nitrogen. For all other runs, throughout the entire work, the carrier gas was hydrogen. The chromatographic analyses for runs with n-butyraldehyde and ethylene or propionaldehyde mixtures were carried out with column A alone.

3.2. RESULTS.

The analytical results for the photolysis of pure n-butyraldehyde alone are given in Table 3.1. For runs 1 to 13 the analysis was made for total non-condensable fraction (H_2 + CO + CH_4), propane, propylene and n-hexane.

For runs 18-52 analysis was carried out for hydrogen, carbon monoxide, methane, ethylene, ethane, propylene, propane and n-hexane with minor exceptions (hydrogen analysis was started after run 21).

These results may be satisfactorily interpreted in terms of the following reaction scheme, which takes account of work reported in the literature as well as the present investigation.

$$C_3H_7\cdot CHO + h\nu \begin{cases} = C_3H_7 + CHO & (a) \\ = C_3H_8 + CO & (b) \\ = C_2H_4 + CH_3\cdot CHO & (c) \\ = CH_3 + C_2H_4\cdot CHO & (d) \end{cases}$$

$$2C_3H_7 = C_6H_{14} \quad (1)$$

$$2C_3H_7 = C_3H_8 + C_3H_6 \quad (2)$$

$$C_3H_7 + C_3H_7\cdot CHO = C_3H_8 + C_3H_7\cdot CO \quad (3)$$

$$C_3H_7CO = C_3H_7 + CO \quad (3a)$$

$$C_3H_7 + C_3H_7\cdot CHO = C_3H_8 + C_3H_6\cdot CHO \quad (4)$$

$$C_3H_6\cdot CHO = C_3H_6 + HCO \quad (4a)$$

$$HCO + C_3H_7\cdot CHO = H_2CO + C_3H_7\cdot CO \quad (4b)$$

$$HCO = H + CO \quad (4c)$$

$$H + C_3H_7\cdot CHO = H_2 + C_3H_7\cdot CO \quad (4d)$$

$$C_3H_7 = CH_3 + C_2H_4 \quad (5)$$

$$CH_3 + C_3H_7\cdot CHO = CH_4 + C_3H_7\cdot CO \quad (5a)$$

$$2CH_3 = C_2H_6 \quad (5b)$$

$$C_3H_7 = H + C_3H_6 \quad (6)$$

The Primary Process (a), (b), (c), (d). Most of the available information on the nature of the primary process comes from the work of Leighton, Levanas, Blacet and Rowe[111], and Blacet and Calvert[112]. They studied the photolysis both in the presence and absence of iodine with essentially monochromatic light of a variety of wavelengths. The work with iodine should give direct evidence on the relative importance of the different primary processes, but it is possible that the heavy atoms selectively de-activate the excited butyraldehyde molecules. Work on the photolysis of acetone in the presence of iodine is of interest in this connection[113]. Rather a high proportion of ethylene was found in the present work at low temperatures. This indicates that process (c) is important, accounting for about 40% of the quantum yield.

It may also be seen from the results that very little methane or ethane was found at low temperatures. (d) can therefore only account for 2 or

3% of the quantum yield.

(a) and (b) are probably of about equal importance as primary processes. These rather rough results correspond fairly well with those to be expected for light of about 2700 Å. This is a reasonable value for the mean effective wavelength of the photolytic light in the present experiments.

The Combination of n-Propyl Radicals (1) is the source of n-hexane in the products formed according to the equation

$$R_{C_6H_{14}} = k_1[C_3H_7]^2$$

where R_X = rate of formation of X.

The value of k_1 was assumed throughout to be

$$k_1 = 10^{14\cdot0} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}.$$

The Disproportionation of n-Propyl Radical (2). From equation (2) it follows that

$$R_{C_3H_6}(2) = k_2[C_3H_7]^2$$

where $R_{C_3H_6}(2)$ is the rate of formation of C_3H_6 from reaction (2). Therefore combining this with the previous expression gives

$$k_2/k_1 = R_{C_3H_6}(2)/R_{C_6H_{14}} \quad .. \qquad .. \quad I$$

From Table 3.1. it may be seen that the ratio of rate constants expressed above is constant (0·16) within experimental error between 25 and 191°C. and is independent of aldehyde pressure and light intensity. These results are expressed graphically in figure 3.1. from which $E_2 - E_1 = 0$, and $A_2 = 0\cdot16\ A_1$. Therefore

$$k_2 = 10^{13\cdot20} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

This result does not agree very well with that of Blacet and Calvert[112] on the photolysis of n-butyraldehyde. They obtained a value of 0·1 at 25°C.

The Abstraction of Hydrogen Atoms from Butyraldehyde (4). Above

191°C. the rate of production of propylene increased rapidly and became much greater than could be attributed to disproportionation. Yet the temperature was too low for the decomposition of the propyl radical (reaction 6) to be significant. The formation of the extra propylene may be satisfactorily explained in terms of reactions (4) and (4a). The quantitative treatment was as follows:

$$C_3H_6(4a) = C_3H_6(\text{total}) - C_3H_6(2).$$

Since $C_3H_6(2) = 0{\cdot}16\ C_6H_{14}$, $C_3H_6(4a)$ may be readily determined by subtraction.

$$R_{C_3H_8}(4) = R_{C_3H_6}(4a) = k_4[C_3H_7][C_3H_7{\cdot}CHO]$$

$$\therefore\ k_4/k_1^{\frac{1}{2}} = R_{C_3H_6(4a)}/R^{\frac{1}{2}}_{C_6H_{14}}[C_3H_7{\cdot}CHO] \ldots \qquad \ldots \text{II}$$

The values of $k_4/k_1^{\frac{1}{2}}$ obtained in this way are given in Table 3.1. and plotted in figure 3.1. Variations of the concentrations of aldehyde and propyl by more than a factor of two caused the predicted alteration in the products of the reaction. From the Arrhenius plot (4) we have

$$k_4 = 10^{11{\cdot}3} \exp.(-10800/RT)\ \text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}$$

Reaction (4b) must be postulated as well as (4c) because the yield of hydrogen was always lower than that of propylene. A calculation of the thermochemistry of reaction (4b) cannot be made with certainty, since there is considerable doubt about the strengths of bonds in aldehydes. A reasonable indication that the reaction may be fairly exothermic can be obtained, however, by considering the reaction

$$HCO + CH_3{\cdot}CHO = H_2CO + CH_3{\cdot}CO \qquad (4e)$$

From thermochemistry we have

$$\Delta H(4e) = \Delta H_f^\circ(H_2CO) + \Delta H_f^\circ(CH_3{\cdot}CO) - \Delta H_f^\circ(HCO) - \Delta H_f^\circ(CH_3{\cdot}CHO)$$

and $\Delta H_f^\circ(H_2{\cdot}CO) = -27{\cdot}7$ k.cal., $\Delta H_f^\circ(CH_3{\cdot}CHO) = -37{\cdot}4$ k.cal.

$\Delta H_f^\circ(CH_3{\cdot}CO)$ and $\Delta H_f^\circ(H{\cdot}CO)$ may be calculated as follows:

$$CH_3 \cdot CO \cdot CH_3 = CH_3 \cdot CO + CH_3$$

$$\therefore D(CH_3 \cdot CO - CH_3) = \Delta H_f^\circ(CH_3 \cdot CO) + \Delta H_f^\circ(CH_3) - \Delta H_f^\circ((CH_3)_2 \cdot CO)$$

and $D(CH_3 \cdot CO - CH_3) = 72$ k.cal., $\Delta H_f^\circ(CH_3) = 32{\cdot}5$ k.cal., $\Delta H_f^\circ((CH_3)_2 \cdot CO) = -51{\cdot}8$ k.cal.

$$\therefore \Delta H_f^\circ(CH_3 \cdot CO) = 72 - 32{\cdot}5 - 51{\cdot}8 = -12{\cdot}3 \text{ k.cal.}$$

$$H \cdot CO = H + CO$$

$$\therefore D(H - CO) = \Delta H_f^\circ(H) + \Delta H_f^\circ(CO) - \Delta H_f^\circ(H \cdot CO)$$

and $D(H - CO) = 14$ k.cal., $\Delta H_f^\circ(H) = 52$ k.cal., and $\Delta H_f^\circ(CO) = -27$ k.cal.

$$\therefore \Delta H_f^\circ(H \cdot CO) = 52 - 27 - 14 = +11 \text{ k.cal.}$$

Hence substituting these values in the expression above, we have for the heat of reaction (4e)

$$\Delta H(4e) = -27{\cdot}7 - 12{\cdot}3 - 11 + 37{\cdot}4$$

$$\simeq -14 \text{ k.cal.}$$

An estimation of the activation energy for reaction (4b) may also be made. The decomposition of the formyl radical should be written:

$$H \cdot CO + M = H + CO + M \qquad (4c)$$

where M is a third body, which must be the aldehyde in this case. Since H·CO is a very simple molecule it is reasonable to suppose that

$$k_{(4c)} = 10^{13{\cdot}5}\, e^{-14000/RT}$$

and for reaction (4b) we have

$$k_{(4b)} = 10^{11}\, e^{-E(4b)/RT}.$$

Now at $10^3/T^\circ A = 2$, $E_{(4b)}$ must be sufficiently low that $k_{(4b)} > k_{(4c)}$. If $k_{(4b)} = 10k_{(4c)}$ we have

$$10^{11}\, e^{-E(4b)/RT} = 10^{14{\cdot}5}\, e^{-14000/RT}$$

$$\therefore \frac{14000 - E(4b)}{2{\cdot}303\, RT} = 3{\cdot}5.$$

If $14000 - E_{(4b)} = x$, then

$$\frac{2x}{4 \cdot 575} = 3 \cdot 5$$

and $$x \simeq 8 \text{ k.cal.mole}^{-1}$$

$\therefore$ $E_{(4b)}$ should not be greater than 6 k.cal.mole^{-1}. This is possible but not highly probable.

The Abstraction of Hydrogen from Butyraldehyde (3). It would be expected that the aldehydic hydrogen would be much the more reactive hydrogen in butyraldehyde because acetaldehyde is much more reactive towards methyl radicals than is the majority of compounds[7]. Furthermore, Birrell and Trotman-Dickenson[101] have shown that the butyraldehydes react with methyl at almost exactly the same rate as do acetaldehyde and propionaldehyde. In this work the rate of attack of propyl on butyraldehyde has been taken to be equal to

$$R_{C_3H_8} - R_{C_3H_6}(4a) - R_{C_3H_6}(2)$$

as is required by the mechanism. At low temperatures this is effectively

$$R_{C_3H_8} - R_{C_3H_6}.$$

Hence it follows that

$$k_3/k_1^{\frac{1}{2}} = (R_{C_3H_8} - R_{C_3H_6})/R^{\frac{1}{2}}_{C_6H_{14}}\left[C_3H_7 \cdot CHO\right] \quad .. \quad .. \text{ III}$$

In this expression as in the analogous one for reaction (4) $\left[C_3H_7 \cdot CHO\right]$ refers to the mean concentration of the aldehyde, as calculated from the rate of formation of carbon monoxide. In extreme cases 40% of the aldehyde was consumed.

The Arrhenius plot (3) in figure 3.1. for results obtained between 98 and 361°C. yields

$$k_3 = 10^{11 \cdot 3} \exp.(-6700/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

Measurement[112] of the temperature coefficient of the quantum yield for carbon monoxide formation in the photolysis of n-butyraldehyde suggested[114] that

$E_3 - E_1^{\frac{1}{2}} = 5{\cdot}6$ k.cal.mole^{-1}. The original authors did not stress this tentative interpretation. It is not surprising that the present work yields a higher value.

The Decomposition of n-Propyl to Ethylene (5). The decomposition of n-propyl to ethylene and methyl may be followed either by determining the ethylene or the (methane plus ethane) formed. Both methods have been employed here. Empirical corrections for the small amounts of methane and ethane formed from the primary photolytic process were applied.

From reactions (5), (5a) and (5b)

$$R_{C_2H_4} = R_{(CH_4 + 2C_2H_6)} = k_5 \left[C_3H_7\right]^2$$

and, as before, it may be shown that

$$k_5/k_1^{\frac{1}{2}} = R_{C_2H_4}/R^{\frac{1}{2}}_{C_6H_{14}} = R_{(CH_4 + 2C_2H_6)}/R^{\frac{1}{2}}_{C_6H_{14}} \quad .. \quad IV$$

The values of this ratio of rate constants derived by the two methods are shown in Table 3.1. k'_5 refers to the rate constant derived from methane + ethane results. Above 313°C. the hexane formed a very small portion of the products. Its amount was therefore determined by measuring the rate of formation of propane and using relationships II and III as follows:

$$k_3/k_1^{\frac{1}{2}} = \left(R_{C_3H_8} - R_{C_3H_6}(4a) - R_{C_3H_6}(2) \right)/\left[C_3H_7 \cdot CHO\right] R^{\frac{1}{2}}_{C_6H_{14}} \quad .. \quad ..II$$

and

$$k_4/k_1^{\frac{1}{2}} = \left(R_{C_3H_6} - R_{C_3H_6}(2) \right)/\left[C_3H_7 \cdot CHO\right] R^{\frac{1}{2}}_{C_6H_{14}} \quad .. \quad III$$

Since the temperature is high $R_{C_3H_6}(2)$ is small in comparison with $R_{C_3H_8}$ and $R_{C_3H_6}(4a)$ and may therefore be neglected. At these high temperatures there is an additional source of propylene other than reactions (2) and (4a) (see (6)) and $R_{C_3H_6}(4a)$ must also be calculated.

Now if $R_{C_6H_{14}}^{\frac{1}{2}} = z$ and $R_{C_3H_6}(4a) = y$ it follows from III. that

$$k_4/k_1^{\frac{1}{2}} = y/[C_3H_7\cdot CHO]\,z$$
$$\therefore\ y = (k_4/k_1^{\frac{1}{2}})[C_3H_7\cdot CHO]\,z.$$

Substituting in II and rearranging gives

$$z = R_{C_3H_8}/(k_4/k_1^{\frac{1}{2}} + k_3/k_1^{\frac{1}{2}})\left[C_3H_7\cdot CHO\right].$$

$k_4/k_1^{\frac{1}{2}}$ and $k_3/k_1^{\frac{1}{2}}$ are found by extrapolation of the appropriate lines and hence z and y are obtained.

From figure 3.1. the rate constant for reaction (5) is given by the expression

$$k_5 = 10^{11\cdot7}\ \text{exp.}(-25200/RT)\ \text{sec.}^{-1}\ \text{from methane}$$
$$k_5 = 10^{11\cdot4}\ \text{exp.}(-25300/RT)\ \text{sec.}^{-1}\ \text{from ethylene.}$$

The results from ethylene have been displaced by 0·1 log units in figure 3.1. As the ethylene may be partially consumed by secondary reactions, the value based on methane is to be preferred.

In the determination of the above rate constant the concentration of aldehyde was maintained approximately constant at about 0·6 μmole cm.$^{-3}$.

A few runs were carried out to determine the effect of pressure on the rate of decomposition of propyl radicals. Increased pressure was obtained in the system by either increasing the initial pressure of the n-butyraldehyde or adding carbon dioxide (~15 μmole cm.$^{-3}$). The results from these runs are shown in Table 3.1., from which it may be seen that the rate constant for reaction (5) was increased under these conditions.

Low n-butyraldehyde pressures were obtained by having a small tapped tube attached to the reaction vessel outlet before the tap leading to the high vacuum line (see figure 2.1.). An aldehyde pressure of the usual order was admitted to the reaction cell and to the small tube and measured on the manometer. The tap separating the cell and tube was closed and the reaction cell was completely pumped out. The tap from the high vacuum line to the cell

was then closed and the tap separating the tube and cell opened. Knowing the sharing ratio between reaction cell and tube (17·1 : 1) the small pressure of aldehyde in the reaction cell was calculated.

Runs were also carried out with low aldehyde pressures and added carbon dioxide (~ 15 μmole cm.$^{-3}$) as reported in Table 3.1.

The rate constant, k_5 was reduced at low pressure of aldehyde and increased again by the addition of carbon dioxide. However, the apparatus was not well suited to the study of the variation of the rate constant with pressure, so this aspect of the investigation was not carried further.

It has been suggested that it may be possible to carry out low pressure photolyses of n-butyraldehyde and analyse accurately for extremely small quantities of products by having a Lovelock Argon Detector in the chromatography unit. This detector is about a hundred thousand times more sensitive than a thermal conductivity detector.

The Decomposition of n-Propyl to Propylene (6). Above 300°C. the rate of production of propylene begins to rise sharply. This increase can be attributed to the decomposition of the propyl by reaction (6). Hence

$$k_6/k_1^{\frac{1}{2}} = \left(R_{C_3H_6} - R_{C_3H_6}(4a) - R_{C_3H_6}(2) \right) / R^{\frac{1}{2}}_{C_6H_{14}}$$

Again it is necessary to calculate the rate of formation of the hexane from that for propane. The results obtained between 347 and 421°C. are given in Table 3.1. and plotted in figure 3.1. Above 420°C., n-butyraldehyde decomposes inconveniently rapidly so that the range over which results were obtained is restricted. The need to correct for the formation of propylene by two additional reactions does not introduce unreasonable errors as can be seen from figure 3.2. which shows the amount of propylene attributed to each reaction over the range of temperatures. Nevertheless, definite Arrhenius parameters

cannot be found. The most that can be said is that the results are consistent with

$$k_6 = 10^{13\cdot6} \exp.(-35000/RT) \text{ sec.}^{-1}$$

which corresponds to the line drawn in figure 3.1. From the preliminary results it appeared that k_6 was rather less dependent upon pressure than k_5.

The Addition of n-Propyl to Ethylene (7). When ethylene is added to the n-butyraldehyde, reaction (7) takes place

$$C_3H_7 + C_2H_4 = C_5H_{11}. \qquad (7)$$

This is followed by

$$C_5H_{11} + C_3H_7{\cdot}CHO = C_5H_{12} + C_3H_7{\cdot}CO \qquad (7a)$$

which accounts for about 75% of the pentyl radicals if the concentration of the ethylene is double that of the aldehyde. About 10% of the pentyl radicals add a further molecule of ethylene (7b)

$$C_5H_{11} + C_2H_4 = C_7H_{15} \qquad (7b)$$

which reacts to give heptane. A proportional correction is then made to allow for the 1% of the initial radicals which ultimately form nonane.

The remaining pentyl radicals dimerise, combine with propyl and disproportionate. The quantities of these products were small and no attempt was made to determine them. Their amount was estimated (F_1) on the assumption that n-pentyl radicals react like n-propyl radicals. An error of 10% in this estimate leads to an error of only 1% in k_7. Hence, it follows that

$$k_7/k_1^{\frac{1}{2}} = (R_{C_5H_{12}(\text{total})} \times F_1)/R^{\frac{1}{2}}_{C_6H_{14}} \left[C_2H_4\right]$$

where $R_{C_5H_{12}(\text{total})}$ is the sum of the pentyl products, i.e. (n-pentane + n-heptane + estimated nonane) and F_1 is the factor, calculated from n-propyl results, allowing for other pentyl products. The results calculated for this ratio of rate constants are given in Table 3.2.

It may be noted that it is particularly convenient to study the

addition of a radical with an odd number of carbon atoms to ethylene in this way, for the determination is simply based on the measurement of n-pentane, n-hexane and n-heptane.

The rate constant derived from figure 3.1. is given by

$$k_7 = 10^{10\cdot9} \exp.(-6500/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

The Combination of Ethyl and n-Propyl (8). When a mixture of propionaldehyde and n-butyraldehyde is photolysed, n-pentane and n-butane are among the products. They are presumably formed by reactions (8) and (9)

$$C_2H_5 + C_3H_7 = C_5H_{12} \qquad (8)$$

$$C_2H_5 + C_2H_5 = C_4H_{10}. \qquad (9)$$

Hence $$k_8/(k_1k_9)^{\frac{1}{2}} = R_{C_5H_{12}}/(R_{C_4H_{10}}.R_{C_6H_{14}})^{\frac{1}{2}}.$$

The results for this ratio of rate constants are given in Table 3.3. and plotted, (8), in figure 3.1. (see note) from which it is deduced that between 54 and 198°C.

$$k_8/(k_1k_9)^{\frac{1}{2}} = 1\cdot9 \pm 0\cdot2$$

and is independent of temperature within the rather large experimental error.

Note: The ratio is given as $(k_1k_9)^{\frac{1}{2}}/k_8$ in Table 3.3. and in figure 3.1. This is merely for convenience in the diagram.

Notes on Tables 3.1., 3.2., 3.3.

All products are in rates of formation of 10^{12}. mole cm.$^{-3}$ sec.$^{-1}$, and all subsequent calculations involve these units.

$[ALD.]$ refers to the mean concentration of n-butyraldehyde - 10^{6}. mole cm.$^{-3}$

$[C_2H_4]$ refers to the concentration of ethylene-10^{6}. mole cm.$^{-3}$

$[PROP.]$ refers to the concentration of propionaldehyde-10^{6}. mole cm.$^{-3}$

Rate Constant Ratios and units:

$k_3/k_1^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k_4/k_1^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k_5/k_1^{\frac{1}{2}}$ 10^{6}. mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k'_5/k_1^{\frac{1}{2}}$ 10^{6}. mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k_6/k_1^{\frac{1}{2}}$ 10^{6}. mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$: $k_7/k_1^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

C_4H_{10} - n-butane.

C_5H_{12} - n-pentane.

C_6H_{14} - n-hexane.

C_7H_{16} - n-heptane.

CH_4^* refers to methane from reaction (5) corrected for CH_4 from primary photolytic act; correction = $1{\cdot}5 \times 10^{-12}$ mole cm.$^{-3}$ sec.$^{-1}$

$C_2H_6^*$ similarly refers to corrected C_2H_6; correction = $0{\cdot}5 \times 10^{-12}$ mole cm.$^{-3}$ sec.$^{-1}$

(X) indicates calculated value.

F_1 is a factor taking into account combination and disproportionation reactions of n-pentyl radicals. This factor is calculated from results on photolysis of n-butyraldehyde alone for n-propyl radicals.

TABLE 3.2. PHOTOLYSIS OF n-BUTYRALDEHYDE AND ETHYLENE MIXTURES

RUN NO.	TEMP. (°A)	TIME (secs.)	[ALD.]	[C_2H_4]	(H_2 + CO + CH_4)	C_5H_{12}	C_6H_{14}	C_7H_{16}	$C_6H_{14}^{\frac{1}{2}}$	F_1	C_5H_{12} (total)	(C_5H_{12} x F_1)	$k_7/k_1^{\frac{1}{2}}$
67	375	7200	2·31	3·56	38·1	4·55	2·14	-	1·47	1·32	4·55	6·02	1·15
61	394	6000	2·07	3·37	36·7	4·76	2·31	0·688	1·52	1·38	5·56	7·66	1·50
62	412	7200	2·08	3·19	50·2	6·92	1·92	0·928	1·39	1·25	7·99	9·99	2·26
63	435	5400	2·04	4·03	64·2	11·0	1·40	2·15	1·18	1·14	13·7	15·6	3·28
64	450	3660	1·99	5·68	67·5	12·1	0·695	3·94	0·834	1·08	17·9	19·3	4·08
68	467	3600	1·96	3·49	90·0	15·7	0·943	1·57	0·971	1·07	17·5	18·7	5·52

TABLE 3.3. PHOTOLYSIS OF n-BUTYRALDEHYDE AND PROPIONALDEHYDE MIXTURES

RUN No.	TEMP. (°A)	TIME (secs.)	[ALD.]	[PROP.]	(H_2 + CO + CH_4)	C_4H_{10}	C_5H_{12}	C_6H_{14}	(C_4H_{10} x C_6H_{14})	(C_4H_{10} x C_6H_{14})$^{\frac{1}{2}}$	$(k_1.k_9)^{\frac{1}{2}}/k_8$
119	327	3605	1·39	0·830	118	5·23	6·92	2·58	13·5	3·67	0·530
114	364	2400	0·994	1·07	75·5	8·83	8·24	1·65	14·6	3·82	0·462
116	423	3600	1·26	0·825	125	4·46	7·73	3·85	17·2	4·15	0·535
120	471	1800	1·26	0·681	125	3·92	5·50	2·83	11·1	3·33	0·607

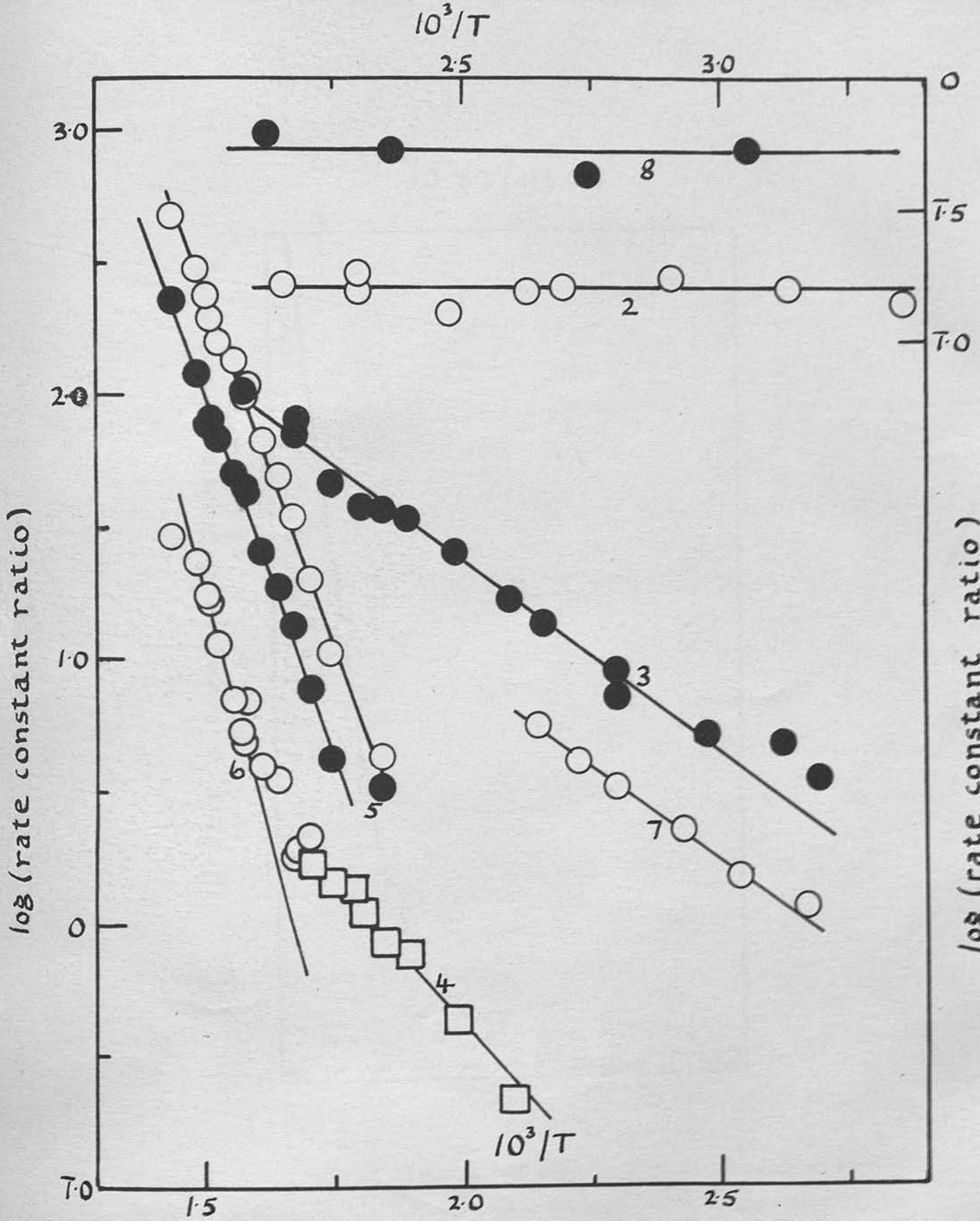


Fig. 3.1. Arrhenius plots for the reactions of n-propyl: 2, disproportionation, k_2/k_1; 8, cross-combination, $(k_1/k_9)^{\frac{1}{2}}/k_8$, the scales at the top right-hand corner refer to these plots; 3, hydrogen abstraction, $(k_3/k_1^{\frac{1}{2}})$; 4, hydrogen abstraction, $(k_4/k_1^{\frac{1}{2}})$; 5, decomposition to methyl and ethylene, $10^6(k_5/k_1^{\frac{1}{2}})$, open circles, results based on methane, filled circles, results based on ethylene; 6, decomposition to propylene and a hydrogen atom, $10^6(k_6/k_1^{\frac{1}{2}})$; 7, addition to ethylene, $(k_7/k_1^{\frac{1}{2}})$.

CHAPTER IV

s-PROPYL RADICALS FROM THE PHOTOLYSIS OF iso-BUTYRALDEHYDE.

Summary. The photoinitiated chain decomposition of iso-butyraldehyde alone and when mixed with ethylene or propionaldehyde has been studied. A mechanism that accounts for the rates of formation of the principal products has been constructed. On the basis that the rate constant for the combination of s-propyl radicals is given by log k = 14, the following Arrhenius parameters of the principal rate-determining reactions have been found:

	log A	E
$2C_3H_7 = C_3H_6 + C_3H_8$	13·82	0
$C_3H_7 + C_3H_7{\cdot}CHO = C_3H_8 + C_3H_7{\cdot}CO$	11·3	6·3
$C_3H_7 + C_3H_7{\cdot}CHO = C_3H_8 + C_3H_6{\cdot}CHO$	11·2	9·5
$C_3H_7 = CH_3 + C_2H_4$	10·6	29·5
$C_3H_7 = H + C_3H_6$	13·8	36·9
$C_3H_7 + C_2H_4 = C_5H_{11}$	11·4	6·9

where k and A are in units of $mole^{-1}$ $cm.^3$ $sec.^{-1}$ or $sec.^{-1}$, and E is in k.cal. $mole^{-1}$. The rate constant for the combination of ethyl and s-propyl is twice the geometric mean of the constants for autocombination.

4.1. EXPERIMENTAL.

Materials. B. D. H. iso-butyraldehyde was shown to be pure by gas chromatographic analysis and no further purification was carried out. Other materials were as previously described.

Apparatus. The apparatus used was identical with that used for

the photolysis of n-butyraldehyde which was described in Chapters II and III. The only minor difference was in the chromatography columns; column A consisted of 150 cm. of 25 - 52 mesh firebrick + 20% dibutyl phthalate and 150 cm. of 25 - 52 mesh firebrick + 20% nitrobenzene.

4.2. RESULTS.

Table 4.1. contains a complete list of the analytical results obtained on the photolysis of iso-butyraldehyde alone, between 20 and 501°C. The products were analysed for carbon monoxide, hydrogen, methane, ethylene, propylene, propane and 2:3-dimethyl butane. No ethane was detected. The results indicate that all the following reactions take place to measurable extent, though others cannot be definitely excluded:

$$(CH_3)_2CH\cdot CHO + h\nu \begin{cases} = C_3H_7 + CHO & (a) \\ = C_3H_8 + CO & (b) \\ = CH_3 + C_2H_4\cdot CHO & (c) \end{cases}$$

$$2C_3H_7 = C_6H_{14} \quad (1)$$

$$2C_3H_7 = C_3H_8 + C_3H_6 \quad (2)$$

$$C_3H_7 + C_3H_7\cdot CHO = C_3H_8 + C_3H_7\cdot CO \quad (3)$$

$$C_3H_7\cdot CO = C_3H_7 + CO \quad (3a)$$

$$C_3H_7 + (CH_3)_2CH\cdot CHO = C_3H_8 + CH_2(CH_3)CH\cdot CHO \quad (4)$$

$$CH_2(CH_3)CH\cdot CHO = C_3H_6 + HCO \quad (4a)$$

$$HCO = H + CO \quad (4b)$$

$$H + C_3H_7\cdot CHO = H_2 + C_3H_7\cdot CO \quad (4c)$$

$$HCO + C_3H_7\cdot CHO = H_2\cdot CO + C_3H_7\cdot CO \quad (4d)$$

$$C_3H_7 + (CH_3)_2CH\cdot CHO = C_3H_8 + (CH_3)_2C\cdot CHO \quad (5)$$

$$(CH_3)_2C\cdot CHO = C_2H_3\cdot CHO + CH_3 \quad (5a)$$

$$CH_3 + C_3H_7\cdot CHO = CH_4 + C_3H_7\cdot CO \quad (5b)$$

$$(CH_3)_2C\cdot CHO = \text{unidentified products} \quad (5c)$$

$$C_3H_7 = CH_3 + C_2H_4 \quad (6)$$

$$C_3H_7 = H + C_3H_6 \quad (7)$$

The Primary Photolytic Act (a), (b), (c). The most complete evidence on the nature of the photolytic act comes from the work of Blacet and Calvert[112]. They studied the products of the photolysis of the pure substance and in mixtures with iodine. With radiation of 2654Å approximately equal numbers of molecules react by (a) and (b), but only one tenth the number react by (c). In the present work very little methane was produced at low temperature. Even below 60°C., considerable quantities of propane are evidently formed by the chain process. The majority of radicals present then must have been formed by (3a) and have been in energetic equilibrium with their environment.

The Combination of s-Propyl (1). No measurements of the rate of combination of s-propyl have been reported although it would seem easier to investigate the photolysis of di-iso-propyl ketone than di-n-propyl ketone by the rotating sector method. Once again a conventional rate constant has been assumed for the purposes of presenting the results

$$k_1 = 10^{14\cdot0} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

The Disproportionation of s-Propyl (2). One molecule of propylene is formed for each pair of propyl radicals that disproportionate. At low temperatures propylene is only formed in this way, therefore

$$k_2 = R_{C_3H_6} / [C_3H_7]^2.$$

But $$k_1 = R_{C_6H_{14}} / [C_3H_7]^2$$

$$\therefore \; k_2/k_1 = R_{C_3H_6}/R_{C_6H_{14}} \; .. \qquad .. \text{ I}$$

The values that have been obtained in this way between 20 and 261°C. are given in Table 4.1. and plotted in figure 4.1. The line (2) may be represented by the equation

$$k_2 = 10^{13\cdot82} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

This rate constant corresponds to a value of $k_2/k_1 = 0{\cdot}65$ that is independent of temperature and was found not to vary when the aldehyde concentration was altered by a factor of five and the intensity of the absorbed light by about the same amount. The agreement with the earlier work on this photolysis[112] ($k_2/k_1 = 0{\cdot}5$ at 25°C.) is not very good.

The Abstraction of Hydrogen Atoms from iso-Butyraldehyde (4). Above 280°C. the rate of production of propylene began to increase rapidly and in a way that could not be explained by disproportionation or by decomposition of the s-propyl radical (reaction 7). Reactions (4) and (4a) appear to account satisfactorily for the propylene in this photolysis, as similar reactions did in the photolysis of n-butyraldehyde. We may write

$$C_3H_6(4a) = C_3H_6\ (\text{total}) - C_3H_6(2)$$

where $C_3H_6(4a)$ is the amount of propylene from reaction (4a). Since $C_3H_6(2) = 0{\cdot}65\ C_6H_{14}$, $C_3H_6(4a)$ may be found by subtraction. Then,

$$R_{C_3H_8(4)} = R_{C_3H_6(4a)} = k_4\left[C_3H_7\right]\left[C_3H_7{\cdot}CHO\right]$$

$$\therefore\ k_4/k_1^{\frac{1}{2}} = R_{C_3H_6(4a)}/R^{\frac{1}{2}}_{C_6H_{14}}\left[C_3H_7{\cdot}CHO\right] \quad .. \qquad .. \text{ II}$$

The values of $k_4/k_1^{\frac{1}{2}}$ obtained in this way are given in Table 4.1. and plotted (4) in figure 4.1. From the Arrhenius plot between 283 and 377°C. the rate constant is given by

$$k_4 = 10^{11{\cdot}2}\ \exp.(-9500/RT)\ \text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}.$$

It is reasonable to suppose that the reaction followed in this way is the removal of a primary hydrogen as this would give a radical likely to decompose into propylene.

Reaction (4d) must be postulated, as in the photolysis of n-butyraldehyde, because of the marked deficiency of hydrogen (from 4c) in the products.

The Abstraction of Hydrogen Atoms from iso-Butyraldehyde (3). The

rate of attack of s-propyl on the aldehydic hydrogen in iso-butyraldehyde has been taken as equal to

$$R_{C_3H_8} - R_{C_3H_6(4a)} - R_{C_3H_6(2)}$$

This is in accord with the proposed mechanism if reaction (5) can be ignored. A comparison of the results in Table 1.6. indicates that k_3 is probably ten or more times k_5. Furthermore, Birrell and Trotman-Dickenson[101] have shown that the butyraldehydes react with methyl at almost exactly the same rates as do acetaldehyde and propionaldehyde. It is therefore reasonable to conclude that the rate of attack on the aldehydic hydrogen is given by

$$k_3/k_1^{\frac{1}{2}} = (R_{C_3H_8} - R_{C_3H_6})/R^{\frac{1}{2}}_{C_6H_{14}} \left[C_3H_7 \cdot CHO\right] \quad .. \quad .. \text{ III}$$

The results obtained by this expression are given in Table 4.1. and plotted in figure 4.1. The rate constant is given by

$$k_3 = 10^{11\cdot3} \exp.(-6300/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

At a given temperature the change of a factor of four in the mean concentration of the aldehyde produced no change in the rate constant.

Reaction (5) may be conveniently considered after reaction (6).

The Decomposition of s-Propyl to Ethylene (6). Above 400°C. considerable quantities of ethylene were formed and the small amount of methane, that was always produced, increased rapidly. These findings could be simply explained only if the s-propyl radical decomposed to methyl and ethylene. We may therefore write:

$$k_6/k_1^{\frac{1}{2}} = R_{C_2H_4}/R^{\frac{1}{2}}_{C_6H_{14}} = R_{CH_4}/R^{\frac{1}{2}}_{C_6H_{14}}.$$

The amounts of hexane were so small that they were estimated from measurements of $R_{C_3H_8}$ and relationships II and III, as for n-propyl radicals. Unfortunately the rate of formation of methane, though rather irreproducable, is consistently about three times the rate of formation of ethylene. This discrepancy is too

great to be attributed to the consumption of the ethylene.

It is possible that the additional methyl leading to methane (reaction 5b) is released by the decomposition of the aldehydic radical (5a). Since the ratio of $k_3 : k_4 : k_5$ will probably vary little between 400 and 500°C., the concentration of $(CH_3)_2C\cdot CHO$ could be proportional to the concentration of propyl. Furthermore, since (5a) is analogous to (6) it is likely that their activation energies are similar. The reaction sequence (5) may therefore be regarded as a reasonable explanation of the findings although there is little direct evidence for it. No useful estimate of k_5 can be made. From the yield of ethylene we have:

$$k_6 = 10^{10.6} \exp.(-29500/RT) \text{ sec.}^{-1}$$

The points and line corresponding to this equation are plotted in figure 4.1.

If the rate constant is calculated from the methane production we have:

$$k'_6 = 10^{10.3} \exp.(-27100/RT) \text{ sec.}^{-1}$$

The line corresponding to this equation is not plotted.

Some doubt is thrown on this interpretation by the work of Heller and Gordon[11] who find that s-propyl radicals from the photolysis of di-iso-propyl ketone decompose to methyl and ethylene with a rate constant of

$$k_6 = 10^{12.03} \exp.(-32500/RT) \text{ sec.}^{-1}$$

Their yields of ethylene and methane were excellently matched and their determination appears reliable. Their values of k_6 were three times those derived in this work from the ethylene analyses but agree well with those based on the methane. Fortunately, the uncertainties as to k_6 do not seriously affect the other conclusions of the present work because they relate only to runs above 400°C.

The Decomposition of s-Propyl to Propylene (7). Reaction (7)

satisfactorily explains the steep rise in the rate of production of propylene between 400 and 500°C. As before,

$$k_7/k_1^{\frac{1}{2}} = (R_{C_3H_6} - R_{C_3H_6(4a)} - R_{C_3H_6(2)})/R^{\frac{1}{2}}_{C_6H_{14}}$$

Again it is necessary to calculate the rate of formation of the hexane from that of the propane. The results are listed in Table 4.1. and plotted on figure 4.1. The need to correct for the formation of propylene by two additional reactions does not introduce unreasonable errors as their contributions are small. The rate constant is given by

$$k_7 = 10^{13\cdot8} \exp.(-36900/RT) \text{ sec.}^{-1}$$

The experiments to determine k_7 were carried out at a concentration of aldehyde of about 0·5 μ mole cm.$^{-3}$. The effect of total pressure on the rate constants for decomposition was not investigated.

The Addition of s-Propyl to Ethylene (8). When ethylene is added to the iso-butyraldehyde, reaction (8) takes place:

$$C_3H_7 + C_2H_4 = C_5H_{11}\cdot \qquad (8)$$

It is followed by

$$C_5H_{11} + C_3H_7\cdot CHO = C_5H_{12} + C_3H_7\cdot CO \qquad (8a)$$

which accounts for about 80% of the iso-pentyl radicals if the concentration of the ethylene is double that of the aldehyde. About 10% of the iso-pentyl radicals add a further molecule of ethylene (8b) and subsequently form 2-methyl hexane. A proportional correction of 1% was made to allow for the iso-pentyl radicals that ultimately form 2-methyl octane. The remaining iso-pentyl radicals presumably dimerise, combine with propyl and disproportionate. The quantities of these products were small, and no attempt was made to analyse for them. Their amount was estimated by making the assumption that iso-pentyl radicals react like s-propyl radicals. An error of 10% in this estimate probably leads to an error of only 1% in k_8. Hence we may write

$$k_8/k_1^{\frac{1}{2}} = \left(R_{C_5H_{12}\ (\text{total})} \times F_2\right)/R^{\frac{1}{2}}_{C_6H_{14}}\left[C_2H_4\right]$$

where $R_{C_5H_{12}\ (\text{total})}$ is the rate of formation of pentyl products (iso-pentane + 2-methyl hexane + calculated 2-methyl octane) and F_2 is the factor, calculated from s-propyl results, allowing for other pentyl products. The results calculated by this method are given in Table 4.2. and plotted in figure 4.1.

$$k_8 = 10^{11\cdot4} \exp.(-6900/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

The Combination of Ethyl and s-Propyl. When a mixture of propionaldehyde and iso-butyraldehyde is photolysed iso-pentane and n-butane are among the products. They are presumably formed by reactions (9) and (10)

$$C_2H_5 + C_3H_7 = C_5H_{12} \qquad (9)$$

$$C_2H_5 + C_2H_5 = C_4H_{10}. \qquad (10)$$

Hence

$$k_9/(k_1k_{10})^{\frac{1}{2}} = R_{C_5H_{12}}/(R_{C_4H_{10}}\ R_{C_6H_{14}})^{\frac{1}{2}}.$$

From the results listed in Table 4.3. and the plot (9) in figure 4.1. it may be deduced that between 50 and 200°C., $k_9/(k_1k_{10})^{\frac{1}{2}} = 2\cdot04$ and is independent of temperature.

Notes on Tables 4.1., 4.2., 4.3.

All products are in rates of formation of 10^{12}. mole cm.$^{-3}$ sec.$^{-1}$, and all subsequent calculations involve these units.

$[\text{ALD.}]$ refers to the mean concentration of iso-butyraldehyde - 10^{6}. mole cm.$^{-3}$

$[C_2H_4]$ refers to the concentration of ethylene - 10^{6}. mole cm.$^{-3}$

$[\text{PROP.}]$ refers to the concentration of propionaldehyde - 10^{6}. mole cm.$^{-3}$

Rate Constant Ratios and units:

$k_3/k_1^{\frac{1}{2}}$ - mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k_4/k_1^{\frac{1}{2}}$ - mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k_6/k_1^{\frac{1}{2}}$ - 10^{6}. mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k'_6/k_1^{\frac{1}{2}}$ - 10^{6}. mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k_7/k_1^{\frac{1}{2}}$ - 10^{6}. mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k_8/k_1^{\frac{1}{2}}$ - mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

C_4H_{10} - n-butane.

C_5H_{12} - iso-pentane.

C_6H_{14} - 2:3-dimethyl butane.

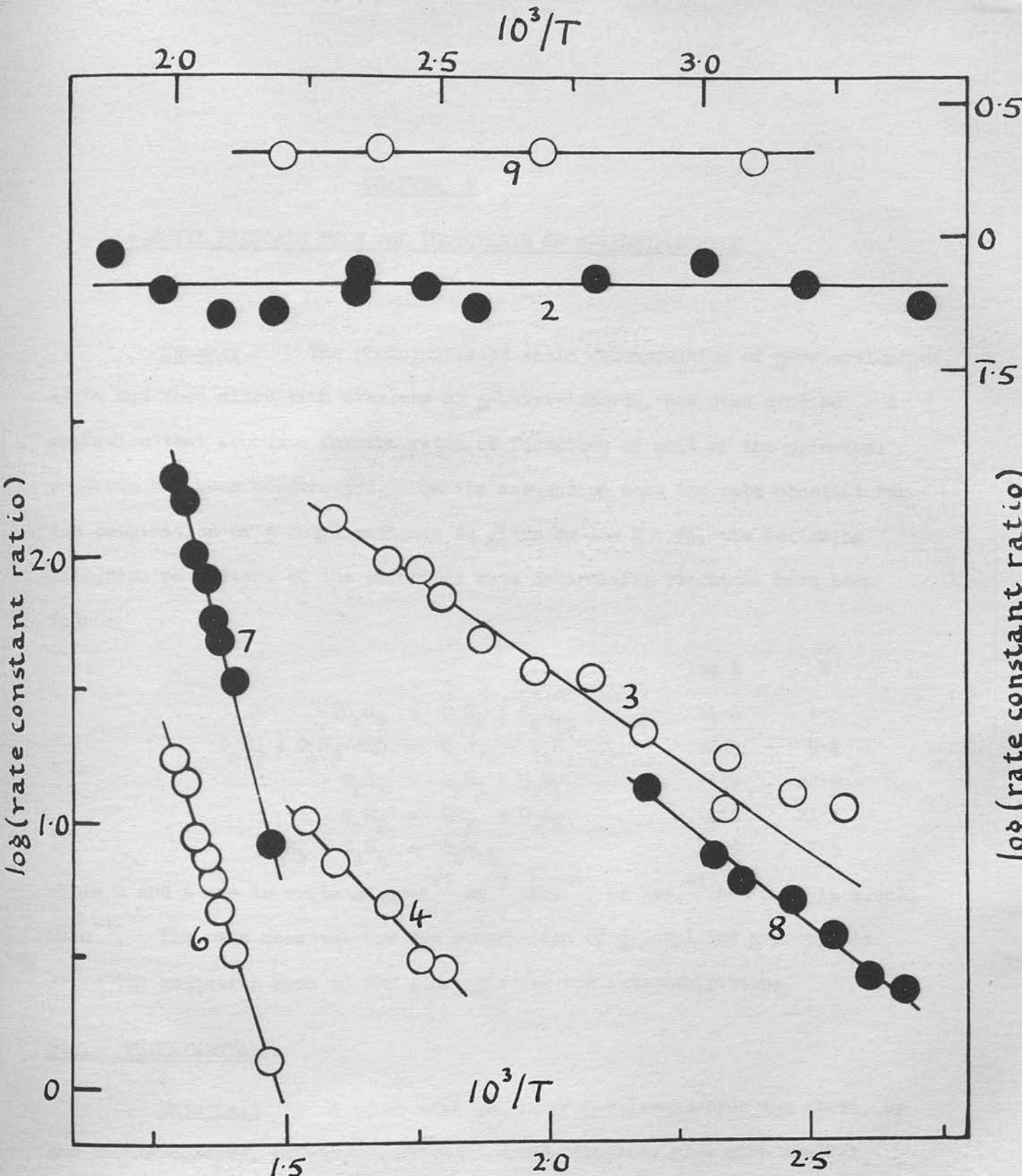
C_7H_{16} - 2-methyl hexane.

(X) indicates a calculated value.

F_2 is a factor taking into account combination and disproportionation reactions of iso-pentyl radicals (cf. F_1 for n-pentyl Table 3.2.).

TABLE 4.3. PHOTOLYSIS OF iso-BUTYRALDEHYDE AND PROPIONALDEHYDE MIXTURES

RUN NO.	TEMP. (^{o}A)	TIME (secs.)	[ALD.]	[PROP.]	(H + CO + CH_4)	C_4H_{10}	C_5H_{12}	C_6H_{14}	(C_4H_{10} x C_6H_{14})	(C_4H_{10} x C_6H_{14})$^{\frac{1}{2}}$	$k_9/(k_1.k_{10})^{\frac{1}{2}}$
117	323	2700	1·76	1·05	101	4·61	12·4	8·89	41·0	6·40	1·94
113	371	3120	0·952	0·919	85·7	5·79	8·79	2·90	16·8	4·10	2·14
115	420	3600	1·30	0·803	126	2·83	7·38	4·33	12·3	3·51	2·10
121	472	1800	1·14	0·748	197	2·61	5·66	3·30	8·61	2·93	1·93



4.1. Arrhenius plots for the reactions of s-propyl: 2, disproportionation, k_2/k_1; 9, s-combination, $k_9/(k_1k_{10})^{\frac{1}{2}}$, the scales at the top right-hand corner refer to these plots; ydrogen abstraction, $(k_3/k_1^{\frac{1}{2}})/\text{mole}^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$; 4, hydrogen abstraction, $(k_4/k_1^{\frac{1}{2}})/$ $^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$; 6, decomposition to methyl and ethylene $10^6(k_6/k_1^{\frac{1}{2}})/\text{mole}^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$ lts based on ethylene; 7, decomposition to propylene and a hydrogen atom, $10^6(k_7/k_1^{\frac{1}{2}})/$ $^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$; 8, addition to ethylene, $(k_8/k_1^{\frac{1}{2}})/\text{mole}^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

CHAPTER V

n-BUTYL RADICALS FROM THE PHOTOLYSIS OF n-VALERALDEHYDE

Summary. The photoinitiated chain decomposition of n-valeraldehyde, alone and when mixed with ethylene or n-butyraldehyde, has been studied. A mechanism that accounts for the rates of formation of most of the principal products has been constructed. On the assumption that the rate constant for the combination of n-butyl radicals is given by log k = 14, the following Arrhenius parameters of the principal rate determining reactions have been found:

	log A	E
$2C_4H_9 = C_4H_8 + C_4H_{10}$	14·6	1·3
$C_4H_9 + C_4H_9\cdot CHO = C_4H_{10} + C_4H_9\cdot CO$	10·9	5·4
$C_4H_9 = C_2H_5 + C_2H_4$	11·2	22·0
$C_4H_9 = CH_3 + C_3H_6$	12·1	27·1
$C_4H_9 + C_2H_4 = C_6H_{13}$	11·1	7·3

where k and A are in units of mole^{-1} cm.^{3} sec.$^{-1}$, or sec.$^{-1}$ and E is in k.cal. mole^{-1}. The rate constant for the combination of n-butyl and n-propyl is twice the geometric mean of the constants for the autocombinations.

5.1. EXPERIMENTAL.

Materials. A commercial sample of n-valeraldehyde was shown, by gas chromatography, to contain about 5% of one impurity plus much smaller amounts of two other impurities. A few grams of this product were purified on a large scale chromatographic column, and it was found that the same results were obtained by either photolysing the purified aldehyde or the original

commercial sample.

Apparatus. Modifications to the general scheme were as follows: the 125 W. lamp was used throughout; the chromatographic column A consisted of 150 cm. of 25 - 52 mesh powdered firebrick plus 10% dimethyl phthalate; column B consisted of 150 cm. of activated alumina impregnated with 1% squalane; the flow rate of carrier gas was about 25 $cm.^3$/minute; the condensable gases were transferred from traps T_1, T_2 and T_3 by means of a pump-down liquid oxygen trap.

5.2. RESULTS.

Twenty-two runs were carried out in which the photoinitiated chain decomposition of n-valeraldehyde was studied between 61 and 416°C. As shown in Table 5.1. the products were analysed for carbon monoxide, hydrogen, methane, ethane, ethylene, propane, propylene, n-butane, 1-butene and n-octane. These results show that all the reactions listed below occur during the photolysis. Deductions may be made about the rate constants of the reactions distinguished by a simple number. Other reactions certainly occur, as will be indicated where appropriate, but little or nothing can be said about their rate constants. All reaction systems involving large radicals and molecules are complicated. This photolysis is no exception. Additional experiments with isotopic tracers and in the presence of substances such as nitric oxide and iodine are needed to elucidate fully the reaction scheme.

$$C_4H_9\cdot CHO + h\nu = C_4H_9 + CHO \quad (a)$$

$$HCO = H + CO \quad (b)$$

$$2C_4H_9 = C_8H_{18} \quad (1)$$

$$2C_4H_9 = C_4H_8 + C_4H_{10} \quad (2)$$

$$C_4H_9 + C_4H_9\cdot CHO = C_4H_{10} + C_4H_9\cdot CO \quad (3)$$

$$C_4H_9\cdot CO = C_4H_9 + CO \quad (3a)$$

$$C_4H_9 = C_2H_5 + C_2H_4 \quad (4)$$

$$C_2H_5 + C_4H_9\cdot CHO = C_2H_6 + C_4H_9\cdot CO \quad (4a)$$

$$C_4H_9 = CH_3 + C_3H_6 \quad (5)$$

$$CH_3 + C_4H_9\cdot CHO = CH_4 + C_4H_9\cdot CO \quad (5a)$$

$$CH_3 + C_2H_5 = C_3H_8 \quad (5b)$$

The Photolytic Act (a) The photolysis of n-valeraldehyde would be most convenient as a source of n-butyl if all the molecules photolysed yielded a butyl radical. At 60°C. the yields of n-butane, 1-butene and n-octane indicate that about one-third of the molecules that produce carbon monoxide on photolysis yield a butyl radical. It appears that photolysis also yields methyl and ethyl radicals, ethylene and rather large amounts of propylene. Only the propylene is surprising in comparison with the initial products of the photolysis of n-butyraldehyde[a]. The photolysis of 1-methyl butyraldehyde[25] does not yield propylene at low temperatures.

The Combination of n-Butyl Radicals (1) is the source of the n-octane in the products formed according to the equation:

$$R_{C_8H_{18}} = k_1 \left[C_4H_9\right]^2.$$

The conventional rate constant

$$k_1 = 10^{14\cdot0} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

has been assumed for the purposes of presenting the results.

The Disproportionation of n-Butyl Radicals (2). The runs carried out between 61 and 229°C. provide direct information on k_2. The range of aldehyde pressure was restricted by the low volatility of n-valeraldehyde. The number of radicals disproportionating was taken as equal to twice the quantity of butene found at the end of the run. Hence

$$k_2/k_1 = R_{C_4H_8}/R_{C_8H_{18}}.$$

Values of this ratio of rate constants are given in Table 5.1. and plotted in figure 5.1., from which we obtain $E_2 - E_1 = 1{\cdot}3$ k.cal.mole^{-1}, and $A_2 = 4A_1$. Therefore

$$k_2 = 10^{14{\cdot}6} \exp.(-1300/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

As mentioned in section 1.3., it is felt that the temperature coefficient found for this reaction, is real. It is difficult to see how n-octane could be formed except by the combination of radicals. Butene might have been produced in the primary photolytic act as well as by disproportionation, but if it was, then a negative temperature coefficient would have been expected for k_2/k_1. If butene were formed in the decomposition of an aldehydic radical produced by hydrogen abstraction, a markedly curved Arrhenius plot would be expected.

The Abstraction of a Hydrogen Atom from n-Valeraldehyde (3). The rate of attack of a n-butyl radical on the aldehydic hydrogen in n-valeraldehyde has been computed on the assumption that all the butane that is not formed in disproportionation comes from this attack. Hence we can write:

$$k_3/k_1^{\frac{1}{2}} = (R_{C_4H_{10}} - R_{C_4H_8})/R^{\frac{1}{2}}_{C_8H_{18}} \left[C_4H_9{\cdot}CHO\right].$$

In this expression $\left[C_4H_9{\cdot}CHO\right]$ refers to the mean concentration of the aldehyde. The results obtained in this way are given in Table 5.1. and plotted in figure 5.1., which yields

$$k_3 = 10^{10{\cdot}9} \exp.(-5400/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

It is clear that this procedure overestimates k_3 because some butane must be formed by attack on the alkyl group in the aldehyde. The error introduced is probably small. It is unfortunate that attack on the alkyl group does not appear to yield a distinctive product by which the rate of attack could be directly calculated. The results with n-butyraldehyde indicate that allowance for this secondary source of butane would only reduce log A_3 by 0·05. The affect on E_3 must be negligible. The simplification tends to favour an erroneously high value of E_3, which is, in fact, rather lower than would have been expected. The apparently low value of E_3 can be ascribed either to the high reactivity of n-butyl or to E_1 being greater than zero.

The Decomposition of n-Butyl to Ethylene (4). The decomposition of n-butyl to ethyl and ethylene may be followed either by determining the ethylene or the ethane formed. Both methods have been employed. We can therefore write:

$$k_4/k_1^{\frac{1}{2}} = R_{C_2H_4}/R^{\frac{1}{2}}_{C_8H_{18}} = R_{C_2H_6}/R^{\frac{1}{2}}_{C_8H_{18}}.$$

Corrections were applied for the amounts of ethane and ethylene formed at low temperatures; ethane, 0·478 x 10^{-12} mole cm.$^{-3}$ sec.$^{-1}$ per 1·0 μ mole cm.$^{-3}$ aldehyde concentration and ethylene, 0·711 x 10^{-12} mole cm.$^{-3}$ sec.$^{-1}$ per 1·0 μ mole cm.$^{-3}$ aldehyde concentration. These corrections were mean values obtained from low temperature runs and as may be seen from Table 5.1. made little difference to the final result. At most temperatures the amount of n-octane formed was so low that it could not be measured. It was estimated from the rate of formation of the butane. The aldehyde concentration for these high temperature runs was purposely held constant at about 0·6 μ mole cm.$^{-3}$. Table 5.1. contains the results obtained in this manner and figure 5.1. shows a plot of these results. The remarkably good agreement has been shown by displacing the points derived from the measurements of ethylene by

0·2 log units. The line drawn through the ethane points has been similarly displaced. Therefore

$$k_4 = 10^{11\cdot2} \exp.(-22000/RT) \text{ sec.}^{-1}$$

The Decomposition of n-Butyl to Propylene (5). The decomposition of n-butyl to methyl and propylene may be similarly followed by determining either the methane or the propylene formed. Hence

$$k_5/k_1^{\frac{1}{2}} = R_{CH_4}/R^{\frac{1}{2}}_{C_8H_{18}} = R_{C_3H_6}/R^{\frac{1}{2}}_{C_8H_{18}}.$$

The corrections that had to be applied to the figures for the rate of formation of propylene, to allow for the formation of the propylene, that was presumed to originate in an initial photolytic decomposition, were considerable at the lower temperatures: $10\cdot5 \times 10^{-12}$ mole cm.$^{-3}$ sec.$^{-1}$ per unit (μ mole cm.$^{-3}$) aldehyde concentration. The correction for initial act methane was much smaller: $1\cdot36 \times 10^{-12}$ mole cm.$^{-3}$ sec.$^{-1}$ per unit (μ mole cm.$^{-3}$) aldehyde. It is gratifying that the figures for methane and propylene balance so well. This is shown in Table 5.1. and plotted in figure 5.1. in which one of the lines has again been displaced. We find that

$$k_5 = 10^{12\cdot1} \exp.(-27100/RT) \text{ sec.}^{-1}$$

At high temperatures, as may be seen from Table 5.1. propane was formed in amounts corresponding to about 5% of the carbon monoxide. Some may have been the product of the combination of methyl and ethyl but it seems unlikely that it can all be attributed to this reaction. The mechanism of high temperature reaction is uncertain to this extent.

Addition of n-Butyl to Ethylene (6). When ethylene is added to the n-valeraldehyde, reaction (6) takes place,

$$C_4H_9 + C_2H_4 = C_6H_{13}. \qquad (6)$$

This is followed by

$$C_6H_{13} + C_4H_9\cdot CHO = C_6H_{14} + C_4H_9\cdot CO \qquad (6a)$$

which accounts for about 85% of the hexyl radicals when the concentration of the ethylene is about twice that of the aldehyde. By analogy with propyl radicals, some 10% of the hexyl radicals add a further ethylene, forming octyl which eventually forms n-octane. Because of these reactions the concentration of n-butyl radicals must be deduced from the butane formed. Analysis was only possible for n-butane and n-hexane and not for n-octane, owing to the very long retention time of n-octane in the chromatography columns employed. Hence the n-hexane from butyl addition to ethylene was corrected by 10% to allow for hexyl addition to ethylene and by a further 5% to allow for hexyl radical combinations and disproportionations. Thus we can write

$$k_6/k_1^{\frac{1}{2}} = R_{C_6H_{16}}\,(\text{total}) \,/\, R^{\frac{1}{2}}_{C_8H_{18}} \left[C_2H_4\right]$$

where $R_{C_6H_{16}}\,(\text{total}) = R_{C_6H_{16}}$ + 15% correction.

The results obtained by this method are given in Table 5.2. and plotted in figure 5.1., from which

$$k_6 = 10^{11\cdot1} \exp.(-7300/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

The Combination of n-Butyl and Propyl (7). When a mixture of n-butyraldehyde and n-valeraldehyde was photolysed, n-hexane, n-heptane and n-octane were formed. They were presumably formed by reactions (1), (7) and (8):

$$C_3H_7 + C_4H_9 = C_7H_{16} \qquad (7)$$

$$2C_3H_7 = C_6H_{14}. \qquad (8)$$

Hence $$k_7/(k_1\cdot k_8)^{\frac{1}{2}} = R_{C_7H_{16}}/(R_{C_6H_{14}}\cdot R_{C_8H_{18}})^{\frac{1}{2}}.$$

The results obtained for this ratio of rate constants are calculated in Table 5.3. and plotted in figure 5.1. Hence between 45 and 184°C.

$$k_7/(k_1 \cdot k_8)^{\frac{1}{2}} = 2{\cdot}0 \pm 0{\cdot}2$$

and is independent of temperature.

In a single run with iso-butyraldehyde a ratio of 2·16 was found for n-butyl and s-propyl radicals (see Table 5.4.).

Notes on Tables 5.1., 5.2., 5.3.

All products are in rates of formation of 10^{12}. mole cm.$^{-3}$ sec.$^{-1}$ and all subsequent calculations involve these units.

$[ALD.]$ refers to the mean concentration of n-valeraldehyde - 10^{6}. mole cm.$^{-3}$

$[C_2H_4]$ refers to the concentration of ethylene - 10^{6}. mole cm.$^{-3}$

$[BUTYR.]$ refers to the concentration of n-butyraldehyde or iso-butyraldehyde - 10^{6}. mole cm.$^{-3}$

Rate Constant Ratios and units:

$k_3/k_1^{\frac{1}{2}}$ - mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k_4/k_1^{\frac{1}{2}}$ - 10^{6}. mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k_5/k_1^{\frac{1}{2}}$ - 10^{6}. mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

$k_6/k_1^{\frac{1}{2}}$ - mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$

C_4H_8 - 1-butene

C_4H_{10} - n-butane

C_6H_{14} - n-hexane

C_7H_{16} - n-heptane

C_8H_{18} - n-octane

* indicates rate of formation of product corrected for primary photolytic act.

(X) indicates calculated value.

a.f. = analytical failure.

u = undetectable in chromatogram.

a = unreliable methane analysis, owing to overoxidation.

TABLE 5.4.

C_6H_{14} - 2:3 dimethyl butane

C_7H_{16} - 1 methyl hexane.

TABLE 5.2. PHOTOLYSIS OF n-VALERALDEHYDE AND ETHYLENE MIXTURES

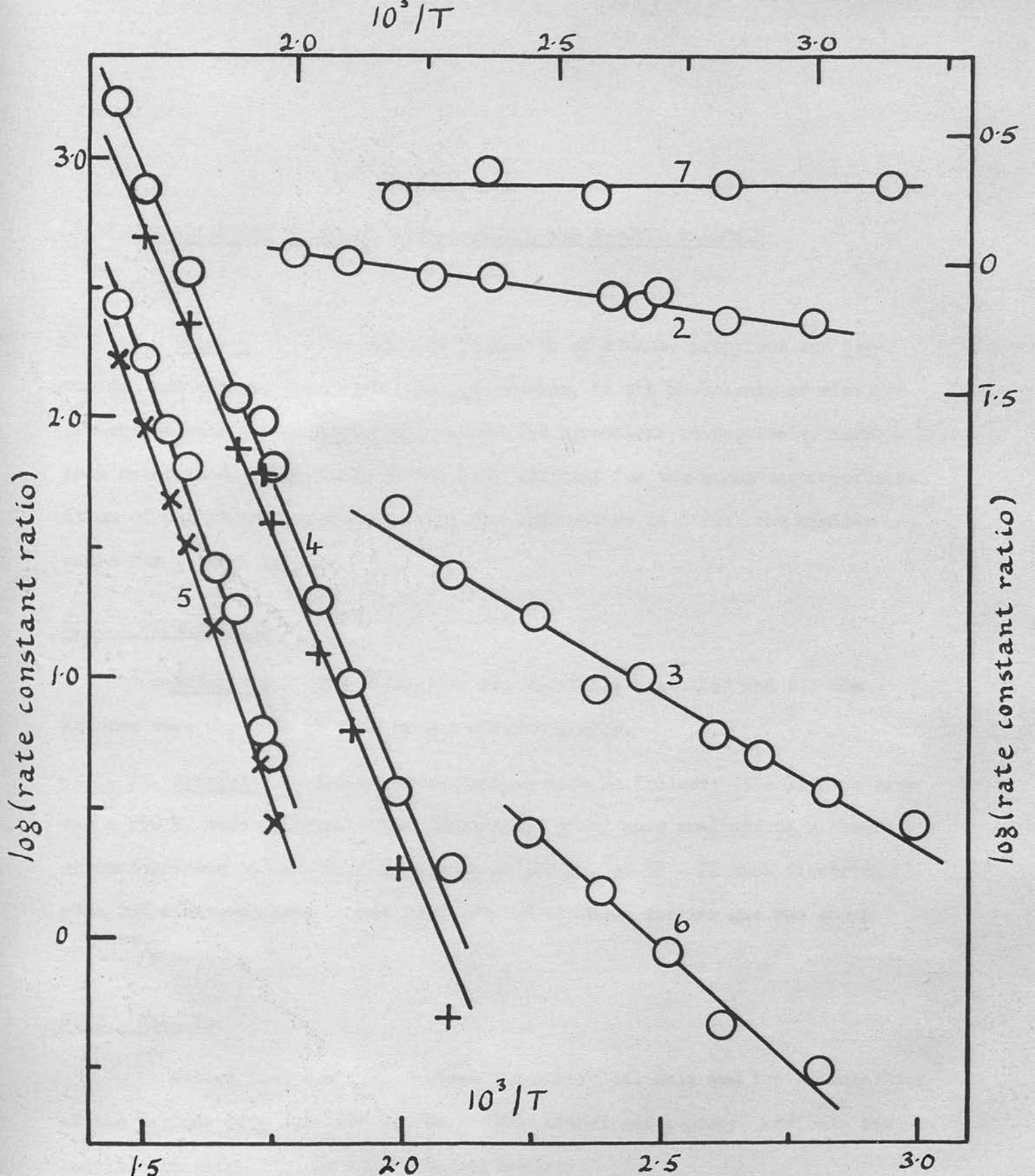
RUN NO.	TEMP. (°A)	TIME (secs.)	[ALD.]	$[C_2H_4]$	$(H_2 + CO + CH_4)$	C_4H_{10}	C_6H_{14}	$k_3/k_1^{\frac{1}{2}}$	$C_8H_{18}^{\frac{1}{2}}$ (calc.)	C_6H_{14} (total)	$k_6/k_1^{\frac{1}{2}}$
176	356	14400	1·28	4·17	13·9	1·89	0·432	3·72	0·397	0·496	0·300
175	382	12000	1·27	3·60	18·5	2·21	0·400	6·17	0·282	0·460	0·454
177	398	10800	1·08	3·50	18·8	1·39	0·418	8·13	0·158	0·481	0·871
174	419	12900	1·19	3·49	23·7	3·37	1·10	11·5	0·246	1·27	1·48
173	445	8700	1·10	3·36	29·7	3·98	1·56	17·0	0·212	1·79	2·51

TABLE 5.3. PHOTOLYSIS OF n-VALERALDEHYDE AND n-BUTYRALDEHYDE MIXTURES

RUN NO.	TEMP. (°A)	TIME (secs.)	[BUTYR.]	[ALD.]	C_6H_{14}	C_7H_{16}	C_8H_{18}	$(C_6H_{14} \times C_8H_{18})$	$(C_6H_{14} \times C_8H_{18})^{\frac{1}{2}}$	$k_7/(k_1k_8)^{\frac{1}{2}}$
165	318	9600	0·909	1·26	0·855	0·859	0·213	0·182	0·426	2·01
163	354	12600	0·885	1·22	0·916	0·874	0·197	0·180	0·424	2·06
161	388	9900	0·993	1·14	0·770	0·917	0·325	0·250	0.500	1·83
164	423	9000	0·588	0·741	0·377	0·421	0·090	0·0339	0·184	2·29
162	457	7500	0·703	1·02	0·430	0·640	0·294	0·126	0·355	1·80

TABLE 5.4. PHOTOLYSIS OF n-VALERALDEHYDE AND iso-BUTYRALDEHYDE MIXTURES

168	315	12600	0·457	1·58	0·597	0·651	0·152	0·0908	0·301	2·16



. 5.1. Arrhenius plots for the reactions of n-butyl: 2, disproportionation, (k_2/k_1); cross-combination, $k_7/(k_1k_8)^{\frac{1}{2}}$, the scales at the top right-hand corner refer to these plots; hydrogen abstraction, $(k_3/k_1^{\frac{1}{2}})/\text{mole}^{-\frac{1}{2}}\ \text{cm.}^{\frac{3}{2}}\ \text{sec.}^{-\frac{1}{2}}$; 4, decomposition to ethyl and ethylene, $(k_4/k_1^{\frac{1}{2}})/\text{mole}^{\frac{1}{2}}\ \text{cm.}^{-\frac{3}{2}}\ \text{sec.}^{-\frac{1}{2}}$, circles, results based on ethane, crosses, results based on ylene; 5, decomposition to propylene and methyl, $10^6(k_5/k_1^{\frac{1}{2}})/\text{mole}^{\frac{1}{2}}\ \text{cm.}^{-\frac{3}{2}}\ \text{sec.}^{-\frac{1}{2}}$, circles, sults based on propylene, crosses, results based on methane; 6, addition to ethylene, $/k_1^{\frac{1}{2}})/\text{mole}^{-\frac{1}{2}}\ \text{cm.}^{\frac{3}{2}}\ \text{sec.}^{-\frac{1}{2}}$

CHAPTER VI

THE REACTIONS OF METHYL WITH s-PROPYL AND t-BUTYL RADICALS

Summary. The rates of formation of ethane, propylene and iso-butane, and ethane, iso-butene and neo-pentane, in the photolysis of mixtures of acetone with methyl iso-propyl ketone and pinacolone respectively, have been determined. The ratio of the rate constant for the cross-disproportionation of methyl and s-propyl to that for combination is 0·22; the similar ratio for t-butyl is 0·70.

6.1. EXPERIMENTAL.

Materials. The pinacolone was carefully distilled and all the ketones were shown to be pure by gas chromatography.

Apparatus. The minor variations were as follows: the light source was a 250 W. mercury lamp. The condensable gases were analysed on a single chromatographic column which consisted of 300 cm. of 52 - 72 mesh firebrick plus 20% dinitrobenzene. The flow rate of hydrogen carrier gas was about 20 $cm.^3$/minute.

6.2. RESULTS.

Tables 6.1. and 6.2. contain the analytical data and the calculations of the various rate constant ratios. With methyl and s-propyl radicals the results are calculated on the following basis:

$$CH_3 + CH_3 = C_2H_6 \quad (1)$$

$$C_3H_7 + C_3H_7 = C_6H_{14} \quad (2)$$

$$CH_3 + C_3H_7 = C_4H_{10} \quad (3)$$

$$2C_3H_7 = C_3H_6 + C_3H_8 \quad (4)$$

$$CH_3 + C_3H_7 = C_3H_6 + CH_4 \quad (5)$$

These reactions are assumed to be the only sources of ethane, propylene, iso-butane and n-hexane in the system. Hence

$$R_{C_2H_6} = k_1 [CH_3]^2$$

$$R_{C_6H_{14}} = k_2 [C_3H_7]^2$$

$$R_{C_4H_{10}} = k_3 [CH_3][C_3H_7].$$

Since propylene is formed both by autodisproportionation (4) and cross-disproportionation (5)

$$R_{C_3H_6} = k_4 [C_3H_7]^2 + k_5 [CH_3][C_3H_7].$$

It was not convenient to measure the rate of formation of n-hexane, which was found by the following method. It may be seen that $k_3/(k_1k_2)^{\frac{1}{2}} = R_{C_4H_{10}}/(R_{C_2H_6} R_{C_6H_{14}})^{\frac{1}{2}}$. Now this ratio may be taken as 2 because all the most reliable determinations of the rates of cross-combination approximate closely to this figure (see Table 1.1.).

Hence $$R_{C_6H_{14}} = R^2_{C_4H_{10}}/4R_{C_2H_6}.$$

$k_4 [C_3H_7]^2$, which is equal to $k_4 R_{C_6H_{14}}/k_2$, is found from the known value of k_4/k_2 of 0·64[b] [11]. $k_5[CH_3][C_3H_7]$ is then found by subtraction and the required ratio from the formula

$$\Delta(\text{Me, s-Pr})^{*} = \frac{k_5}{k_3} = \frac{R_{C_3H_6} - 0{\cdot}64\, R_{C_6H_{14}}}{R_{C_4H_{10}}} \quad \ldots \quad \ldots \text{ I}$$

* See p.21 for notation.

The results obtained in this way are shown in Table 6.1. Those obtained for the cross-disproportionation of methyl and t-butyl by a similar method are shown in Table 6.2. The reaction scheme in this case is:

$$CH_3 + CH_3 = C_2H_6 \quad (1)$$

$$C_4H_9 + C_4H_9 = C_8H_{18} \quad (6)$$

$$CH_3 + C_4H_9 = C_5H_{12} \quad (7)$$

$$2C_4H_9 = C_4H_8 + C_4H_{10} \quad (8)$$

$$CH_3 + C_4H_9 = C_4H_8 + CH_4 \quad (9)$$

Δ (t-Bu, t-Bu) was taken as 4·59 [12].

In all the runs the acetone was in considerable excess. This precaution reduced the size of the second term in the numerator of expression I, which is equal to $C_3H_6(4)$ in Table 6.1. and $C_4H_8(8)$ in Table 6.2. Hence small errors in the rate constant for cross-combination and auto-disproportionation have little effect on the final value of Δ (Me, Alk).

Notes on Tables 6.1., 6.2.

All products are in rates of formation of 10^{12}. mole cm.$^{-3}$ sec.$^{-1}$, and all subsequent calculations involve these units.

$[(CH_3)_2 \cdot CO]$ refers to the concentration of acetone - 10^6. mole cm.$^{-3}$

$[CH_3 \cdot CO \cdot C_3H_7]$ refers to the concentration of methyl iso-propyl ketone - 10^6. mole cm.$^{-3}$.

$[CH_3 \cdot CO \cdot C_4H_9]$ refers to the concentration of pinacolone - 10^6. mole cm.$^{-3}$

C_4H_8 - iso-butene

C_4H_{10} - iso-butane

C_5H_{12} - neo-pentane

C_6H_{14} - 2:3-dimethyl butane

C_8H_{18} - 2:2:3:3-tetramethyl butane.

TABLE 6.1. PHOTOLYSIS OF ACETONE AND METHYL iso-PROPYL KETONE MIXTURES

RUN NO.	TEMP. (°A)	TIME (secs.)	$[(CH_3)_2CO]$	$[CH_3COC_3H_7]$	C_2H_6	C_3H_6	C_4H_{10}	$C_2H_6^{\frac{1}{2}}$	$C_6H_{14}^{\frac{1}{2}}$	C_6H_{14}	$C_3H_6(4)$	$C_3H_6(5)$	k_5/k_3
222	353	1800	2·53	0·930	18·05	3·42	10·9	4·25	1·28	1·64	1·05	2·37	0·218
221	364	1500	2·26	1·06	21·8	3·01	11·1	4·67	1·19	1·42	0·909	2·10	0·189
217	377	1800	2·22	0·865	30·2	3·30	13·4	5·50	1·22	1·49	0·954	2·35	0·175
216	387	2400	1·48	1·05	23·7	3·55	12·6	4·87	1·29	1·66	1·06	2·49	0·198
220	419	1800	1·89	0·920	24·6	3·49	10·5	4·96	1·06	1·12	0·717	2·77	0·264
219	423	1500	1·85	1·00	23·4	4·03	12·1	4·84	1·25	1·56	0·999	3·03	0·254

TABLE 6.2. PHOTOLYSIS OF ACETONE AND PINACOLONE MIXTURES

RUN NO.	TEMP. (°A)	TIME (secs.)	$[(CH_3)_2CO]$	$[CH_3COC_4H_9]$	C_2H_6	C_4H_8	C_5H_{12}	$C_2H_6^{\frac{1}{2}}$	$C_8H_{18}^{\frac{1}{2}}$	C_8H_{18}	$C_4H_8(8)$	$C_4H_8(9)$	k_9/k_7
227	353	1800	4·44	1·19	36·8	10·8	10·4	6·07	0·856	0·733	3·36	7·44	0·715
226	371	2040	4·07	1·14	58·3	10·8	11·2	7·64	0·734	0·539	2·48	8·32	0·743
225	402	2100	3·55	1·08	56·5	10·6	11·9	7·52	0·792	0·627	2·88	7·72	0·650
228	425	1860	3·45	0·973	58·8	9·65	10·9	7·67	0·711	0·506	2·32	7·33	0·672
229	461	1800	3·08	0·903	39·2	9·75	9·75	6·26	0·780	0·608	2·79	6·96	0·715

CHAPTER VII

ETHYL RADICALS FROM THE PHOTOLYSIS OF PROPIONALDEHYDE

Summary. The photoinitiated chain decomposition of propionaldehyde, alone and when mixed with ethylene, has been studied. The amounts of hydrogen, carbon monoxide, methane, ethylene, ethane and n-butane in the products were determined. A mechanism was devised which accounted for the bulk of the products. On the assumption that the rate constant for the combination of ethyl radicals is given by log k = 14, the Arrhenius parameters for the following reactions have been found:

	log A	E
$2C_2H_5 = C_2H_4 + C_2H_6$	13·18	0
$C_2H_5 + C_2H_5{\cdot}CHO = C_2H_6 + C_2H_5{\cdot}CO$	11·1	5·9
$C_2H_5 + C_2H_4 = C_4H_9$	12·05	8·6

where k and A are in mole^{-1} cm.^{3} sec.$^{-1}$ and E is in k.cal.mole^{-1}. The rate constant for the reaction

$$C_2H_5 = H + C_2H_4$$

is 10^2 sec.$^{-1}$ at 464°A and 0·65 μ mole cm.$^{-3}$ concentration of the aldehyde.

7.1. EXPERIMENTAL.

Materials. The propionaldehyde was a commercial sample purified by several bulb to bulb distillations and tested by gas chromatography.

Apparatus. The few modifications to the general scheme were exactly those described in Chapter V.

7.2. RESULTS.

Table 7.1. contains the analytical results obtained for twenty-three runs carried out on the photolysis of propionaldehyde between 50 and 505°C. Product analysis was made for hydrogen, carbon monoxide, methane, ethylene, ethane and n-butane. No other hydrocarbon products were formed. The following reaction mechanism serves as a useful framework for the discussion of the findings:

$$C_2H_5{\cdot}CHO + h\nu \begin{cases} = C_2H_5 + CHO & (a) \\ = C_2H_6 + CO & (b) \\ = C_2H_4 + H_2CO & (c) \\ = CH_3 + CH_2{\cdot}CHO & (d) \end{cases}$$

$$2C_2H_5 = C_4H_{10} \qquad (1)$$

$$2C_2H_5 = C_2H_4 + C_2H_6 \qquad (2)$$

$$C_2H_5 + C_2H_5{\cdot}CHO = C_2H_6 + C_2H_5{\cdot}CO \qquad (3)$$

$$C_2H_5{\cdot}CO = C_2H_5 + CO \qquad (3a)$$

$$C_2H_5 = C_2H_4 + H \qquad (4)$$

$$H + C_2H_5{\cdot}CHO = H_2 + C_2H_5{\cdot}CO \qquad (4a)$$

The Primary Process (a), (b), (c), (d). Blacet and Pitts[24] estimated the relative importance of the four primary photolytic processes, at 30°C. for light of different wavelengths. Similar estimates cannot be accurately made from the present results. As will be seen from Table 7.1. at 50°C. the rates of formation of methane (presumably from the reaction of methyl with the aldehyde) and hydrogen (from the decomposition of the formyl and subsequent reaction of the atom with the aldehyde) were nearly equal. Each was equal to about $2\frac{1}{2}\%$ of the rate of formation of carbon monoxide. Extrapolation from the rates of formation of ethane at higher temperatures indicates that about equal numbers of propionaldehyde molecules decompose to

ethyl (a) and directly to ethane (b). This product distribution is roughly what would be expected for photolysis by light of 2700 Å. A consideration of the absorption curve for the aldehyde, the output of the lamp and the transmission of the quartz shows that this is quite reasonable. The same mean effective wavelength of photolytic light was deduced for n-butyraldehyde. None of the secondary photolytic processes is sufficiently important to necessitate corrections at higher temperatures.

The Combination of Ethyl Radicals (1) is the source of the n-butane in the products which is formed according to the equation

$$R_{C_4H_{10}} = k_1 \left[C_2H_5\right]^2.$$

As given in Chapter 1.2. Shepp and Kutschke[42] obtained a value for the rate constant for this combination of

$$k = 10^{14.5} \exp.(-2000/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

from Rotating Sector studies on the photolysis of diethyl ketone. The Sector Technique can be satisfactorily applied to only the cleanest reaction systems. It therefore seems possible that the temperature coefficient reported may not be real, in spite of the care taken by the investigators. This supposition is supported by the fact that no considerable temperature coefficient has been found for the rate constant ratios for cross-combinations[(a),(b)] which are much easier to measure. Accordingly here, the conventional value

$$k_1 = 10^{14} \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

has been used throughout in addition to the experimental value, which is given in parenthesis.

The Disproportionation of Ethyl (2). Twelve runs that provide direct information on k_2 were carried out between 50 and 310°C. The number of radicals disproportionating was taken as equal to twice the quantity of ethylene found at the end of the run. Values of k_2/k_1 obtained in this way

are given in Table 7.1. and plotted in figure 7.1.

$$E_2 - E_1 = 0, \quad A_2 = 0{\cdot}150\ A_1. \quad \text{Therefore}$$
$$k_2 = 10^{13{\cdot}18};\ \left(10^{13{\cdot}68} \exp.(-2000/RT) \right) \text{ mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}$$

The values of k_2 found are independent of the pressure in the system.

The Abstraction of Hydrogen Atoms from Propionaldehyde (3). The increasing amounts of ethane found at higher temperatures can be ascribed to the abstraction of an aldehydic hydrogen by the ethyl radical. Allowance must be made for the formation of ethane by disproportionation in estimating the extent of this reaction. Hence

$$R_{C_2H_6}(3) = R_{C_2H_6} - R_{C_2H_6}(2)$$

and
$$k_3/k_1^{\frac{1}{2}} = \left(R_{C_2H_6} - R_{C_2H_6}(2) \right) / R^{\frac{1}{2}}_{C_4H_{10}} \left[C_2H_5 \cdot CHO \right].$$

Since $R_{C_2H_6}(2) = R_{C_2H_4}(2)$ and below 315°C. ethylene is only formed by disproportionation, this ratio can readily be evaluated. It is independent of the mean aldehyde concentration between 0·67 and 2·7 μ mole cm.$^{-3}$ at 150°C. The results are given in Table 7.1. and from the Arrhenius plot shown in figure 7.1. we have

$$k_3 = 10^{11{\cdot}1} \exp.(-5900/RT)\ \text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}$$
$$\left(\text{or } 10^{11{\cdot}35} \exp.(-6900/RT)\ \text{mole}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1} \right).$$

Blacet and Pitts[24] suggested that the temperature coefficient for the rate of formation of carbon monoxide in the high temperature photolysis of propionaldehyde was equal to $E_3 - \frac{1}{2}E_1$. Hence they found $E_3 - \frac{1}{2}E_1 = 8{\cdot}1$ k.cal.mole^{-1}. If the assumption is made that their light intensity was constant in the same runs at 3130 Å (their Table III) and that the pressure of aldehyde was also constant, a value of $E_3 - \frac{1}{2}E_1 = 6{\cdot}3$ k.cal.mole^{-1} can be deduced by the treatment outlined here.

Dodd[60] concluded that the effect of temperature on the overall rate

of photo-decomposition of propionaldehyde could not be represented by the Arrhenius equation. On the other hand, Niclause[98] suggested that the correct interpretation of Dodd's work indicated that $E_3 - \frac{1}{2}E_1 = 10$ k.cal.mole^{-1}.

The Decomposition of Ethyl to Ethylene (4). Above 350°C. the rate of formation of ethylene began to rise sharply. This increase can be attributed to the decomposition of the ethyl radical, so we can write

$$k_4/k_1^{\frac{1}{2}} = \left(R_{C_2H_4} - R_{C_2H_4}(2) \right) / R^{\frac{1}{2}}_{C_4H_{10}}.$$

At these temperatures the runs were very short and the amounts of n-butane in the products were usually too small to measure. Its formation was therefore calculated from the rate of formation of ethane and the known values of $k_3/k_1^{\frac{1}{2}}$. $R_{C_2H_4}(2)$ could then be obtained from $R_{C_4H_{10}}$; in practice it could be neglected. It seemed probable that k_4 would depend upon the pressure in the system, therefore the mean aldehyde concentration was held constant at about 0·67 μ mole cm.$^{-3}$. The results obtained by this method are listed in Table 7.1. and the Arrhenius plot in figure 7.1. gives

$$k_4 = 10^{11\cdot2} \exp.(-31000/RT) \text{ sec.}^{-1}$$
$$\left(\text{or } 10^{11\cdot45} \exp.(-32000/RT) \text{ sec.}^{-1} \right).$$

In principle $k_4/k_1^{\frac{1}{2}}$ could be derived from the rate of formation of hydrogen by reaction (4a). However, the determination of small quantities of hydrogen in 20 to 50 times the amount of carbon monoxide is not easy and it is doubtful if the analyses were reliable.

The activation energy found for the decomposition is certainly too low; it should be greater than the endothermicity of the reaction which is 39 k.cal. mole^{-1} if $D(C_2H_5 - H)$ is 98 k.cal. mole^{-1}. The error is at least partially caused by the overestimation of the amounts of n-butane formed at high temperature and hence of the concentration of ethyl radicals. This is clearly shown in Table 7.1. with runs 202, 203 and 204 where the calculated

n-butane exceeded the amount of n-butane measured. Such an overestimation would occur if an additional source of ethane were important at high temperatures. The attack of ethyl radicals on the alkyl group in propionaldehyde would produce ethane. At low temperatures this reaction is unlikely to be important compared with (3), because of its presumably greater activation energy, which is probably at least as great as that for attack of ethyl on diethyl ketone[65]; furthermore, the A factor will be comparatively low. The higher energy of activation would decrease in significance as the temperature is raised. This complication should have little effect on the value obtained for the rate constant at, say, 400°C. The present work yields $\log k_4/\text{sec.}^{-1} = 1{\cdot}2$. Bywater and Steacie[14] who produced ethyl by the mercury photosensitised decomposition of ethane found that $\log k_4/\text{sec.}^{-1} = 1{\cdot}1$ at 400°C. This agreement is far better than could reasonably have been expected and depends largely on the temperature chosen for the comparison. Nevertheless, it encourages the belief that the assumptions underlying both determinations are correct.

The Addition of Ethyl to Ethylene (5). When ethylene is added to the propionaldehyde, reaction (5) takes place

$$C_2H_5 + C_2H_4 = C_4H_9. \qquad (5)$$

This is followed by

$$C_4H_9 + C_2H_5{\cdot}CHO = C_4H_{10} + C_2H_5{\cdot}CO \qquad (5a)$$

and also by

$$C_2H_5 + C_4H_9 = C_6H_{14} \qquad (5b)$$

and

$$C_4H_9 + C_2H_4 = C_6H_{13}. \qquad (5c)$$

The hexyl radicals may form hexane by hydrogen abstraction or add a further ethylene to give an octyl radical. This system is not as simple as that for the addition of propyl radicals to ethylene because the critical products can be formed by different routes. Hence the interpretation of the analytical

determinations of ethane, n-butane and n-hexane are not as certain as would be wished. The results were treated as follows: from $R_{C_2H_6}$ the concentration of ethyl and $R_{C_4H_{10}}(1)$ are found from the known values of $k_3/k_1^{\frac{1}{2}}$. Then

$$R_{C_4H_{10}}(5a) = R_{C_4H_{10}} - R_{C_4H_{10}}(1).$$

Each molecule of hexane, whether it is formed by (5b) or (5c) corresponds to the addition of an ethyl radical to ethylene. Hence, the rate of addition of ethyl to ethylene = $R_{C_4H_{10}}(5a) + R_{C_6H_{14}}$. This expression may not be complete because some of the original butyls may finish up as octanes or higher hydrocarbons. An indication of the importance of such additional reactions can be obtained by apportioning the hexane between reactions (5b) and (5c). This can be done if it is assumed that n-butyl radicals react with propionaldehyde at the same rate as they do with n-valeraldehyde[c]. This assumption is supported by the observation that methyl radicals react with the two aldehydes at identical rates[101]. Hence, from the rate of formation of n-butane by reaction (5a) the steady state concentration of n-butyl and the rate of formation of n-octane $R_{C_8H_{18}}$(comb.) can be found. The $R_{C_6H_{14}}(5b)$ is then the geometric mean of the rates of formation of n-butane and n-octane[f]. In all cases $R_{C_8H_{18}}$(comb.) is small and can hereinafter be neglected. Two series of runs were carried out. In the first series, α, the ratio of aldehyde to ethylene concentration was 1:1 and $R_{C_6H_{14}}(5b)$ was within experimental error equal to $R_{C_6H_{14}}$. When the ratio was 1:2, β, $R_{C_6H_{14}}(5b)$ was considerably lower than $R_{C_6H_{14}}$. Under these conditions it is probable that considerable amounts of octane were formed from n-hexyl. In the first instance the expression

$$k_5/k_1^{\frac{1}{2}} = \left(R_{C_4H_{10}}(5a) + R_{C_6H_{14}} \right) / R^{\frac{1}{2}}_{C_4H_{10}}(1) \left[C_2H_4 \right]$$

will be adequate; in the second, the expression will lead to a low value of k_5. Values of $k_5/k_1^{\frac{1}{2}}$ obtained in both series of experiments are given in

Table 7.2. and plotted in figure 7.1. The ratio of aldehyde to ethylene has little effect on the activation energy but clearly lowers the apparent rate constant. Two additional runs (series γ) with higher ethylene concentrations yielded still lower values of $k_5/k_1^{\frac{1}{2}}$. The line 5α corresponds to

$$k_5 = 10^{12.1} \exp.(-8600/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

$$\left(\text{or } 10^{12.35} \exp.(-9600/RT) \text{ mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1} \right).$$

C_4H_{10}	k_2/k_1	C_2H_6-C_2H_4(2)	$C_4H_{10}^{\frac{1}{2}}$	$k_3/k_1^{\frac{1}{2}}$	C_2H_4(2)	C_2H_4(4)	$k_4/k_1^{\frac{1}{2}}$
13·0	0·136	-	-	-	-	-	-
13·7	0·144	-	-	-	-	-	-
16·0	0·159	54·9	4·00	3·97	-	-	-
16·6	0·152	56·9	4·07	4·89	-	-	-
10·8	0·156	46·1	3·29	7·45	-	-	-
12·85	-	97·6	3·58	11·1	-	-	-
3·56	0·148	14·7	1·89	11·6	-	-	-
14·9	0·149	95·9	3·86	9·30	-	-	-
7·10	0·154	47·0	2·66	15·8	-	-	-
7·08	0·150	58·4	2·66	23·0	-	-	-
5·05	-	75·9	2·25	26·1	-	-	-
7·15	0·151	199	2·67	41·5	-	-	-
3·77	0·150	101	1·94	74·0	-	-	-
2·82	0·155	153	1·68	114	-	-	-
3·14	-	133	1·77	96·9	-	-	-
5·72	-	-	2·68(X)	97·7	1·08	1·61	0·600?
a.f.	-	-	2·29(X)	126	0·786	0·89	0·380
2·82	-	-	2·60(X)	135	1·02	0·86	0·331
1·77	-	-	2·49(X)	151	0·932	3·78	1·52
t	-	-	2·27(X)	186	0·773	5·29	2·33
u	-	-	2·80(X)	229	1·18	21·6	7·72
u	-	-	3·95(X)	282	2·34	56·0	14·2
u	-	-	4·30(X)	347	2·78	113	26·4

TABLE 7.2. PHOTOLYSIS OF PROPIONALDEHYDE AND ETHYLENE MIXTURES

RUN NO.	TEMP. (°A)	TIME (secs.)	[ALD.]	$[C_2H_4]$	$(H_2 + CO + CH_4)$	C_2H_6	C_4H_{10}	C_6H_{14}	$C_4H_{10}^{\frac{1}{2}}(1)$	$C_4H_{10}(1)$	$C_4H_{10}(5a)$	$C_8H_{18}^{\frac{1}{2}}$ (comb.)	$C_6H_{14}(5b)$	$C_4H_{10}(5a) + C_6H_{14}$	$k_5/k_1^{\frac{1}{2}}$
SERIES α															
215	376	3000	1·49	1·54	40·9	22·1	14·2	1·66	3·21	10·3	3·90	0·476	3·05	5·56	1·13
213	410	2100	1·65	1·73	62·1	39·3	18·1	3·60	2·77	7·67	10·4	0·691	3·84	14·0	2·92
214	461	1800	1·14	1·14	82·4	49·3	24·4	4·40	2·24	5·00	19·4	1·11	5·08	23·8	9·35
SERIES β															
206	379	2700	1·78	3·46	49·1	28·6	14·8	6·23	3·29	10·8	4·00	0·450	2·88	10·2	0·90
211	410	2400	0·987	1·71	37·5	18·8	11·8	2·78	2·20	4·84	6·96	0·705	3·10	9·74	2·59
207	448	1500	1·13	2·25	72·3	33·1	19·1	5·58	1·92	3·69	15·4	0·783	3·00	21·0	4·86
210	465	1800	1·08	2·20	83·0	39·2	29·5	6·40	1·84	3·39	26·1	1·09	4·02	32·5	8·02
SERIES γ															
212	410	1800	1·01	3·64	41·9	15·4	6·54	3·83	1·77	3·13	3·41	0·344	1·21	7·24	1·12
208	418	1380	0·865	4·04	73·7	25·8	15·1	13·0	2·97	8·82	6·28	0·649	3·86	19·3	1·61

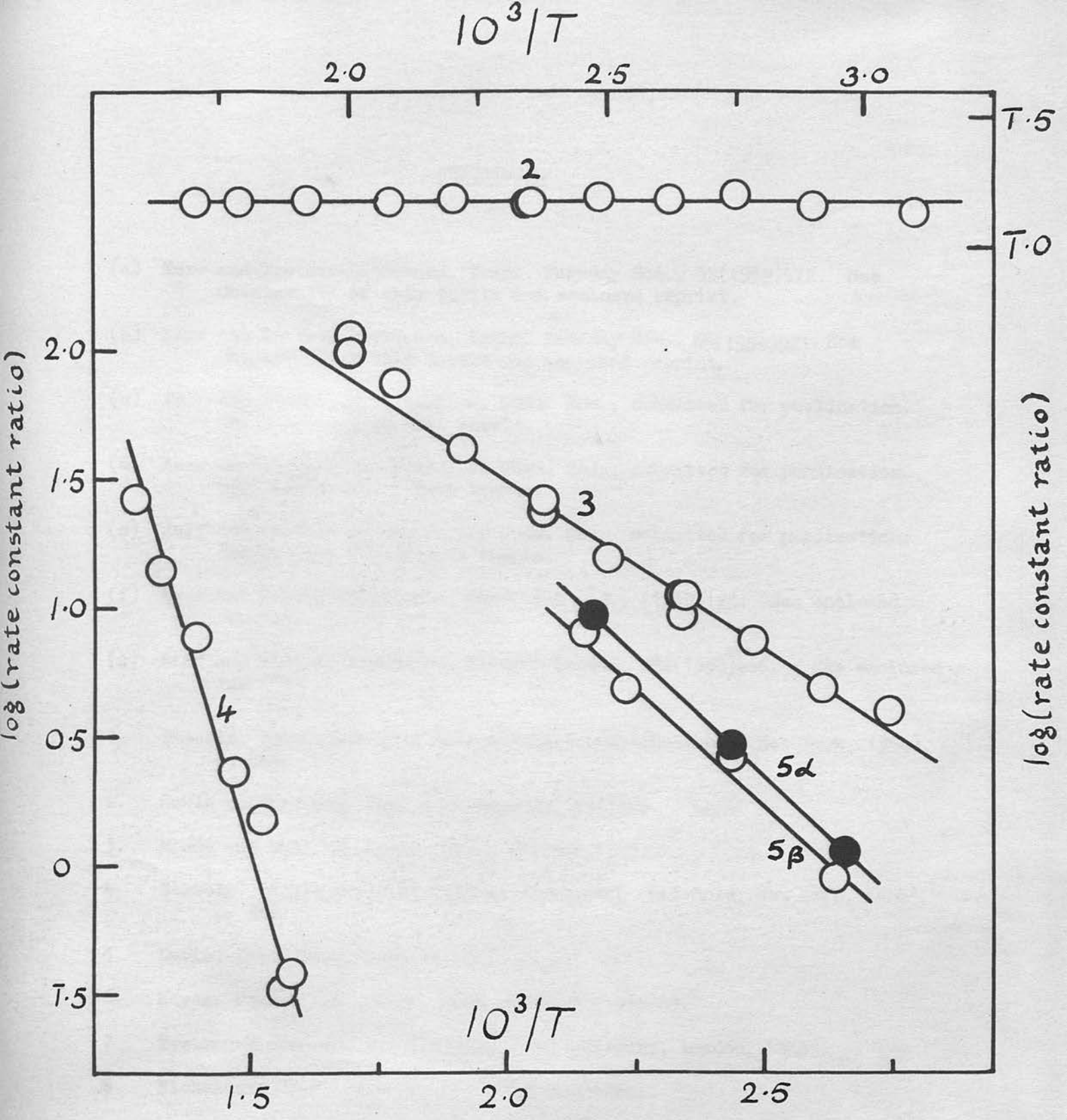


Fig. 7.1. Arrhenius plots for the reactions of ethyl: 2, disproportionation, k_2/k_1; 3, hydrogen abstraction, $(k_3/k_1^{\frac{1}{2}})$/mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$; 4, decomposition to ethylene and a hydrogen atom, $10^6(k_4/k_1^{\frac{1}{2}})$/mole$^{\frac{1}{2}}$ cm.$^{-\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$; 5, addition to ethylene, $(k_5/k_1^{\frac{1}{2}})$/mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$, 5 α, aldehyde: ethylene 1:1, 5 β, aldehyde: ethylene 1:2.

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APPENDIX

Before the experiments on the photolyses of the aldehydes were started, a few runs were carried out on the photolysis of mixtures of acetone and thiols. A note on this work has appeared in the Journal of the Chemical Society and a reprint is enclosed here.

A reprint is also enclosed of a paper on the Decomposition of Nitramide in Anisole. This study was made over a period of years by final honours year students, and this author had the privilege of working on the topic as an undergraduate and of helping in the direction of the work as a graduate. Another paper on the decomposition of Nitramide in m-Cresol has been submitted for publication.

REPRINTS OF PAPERS

(*Reprinted from Nature, Vol.* 182, *p.* 466 *only, August* 16, 1958)

Absorbents for Aldehydes and Olefins

THE usual forms of absorbents for aldehydes, such as ammonia and bisulphite solutions, cannot readily be used in vacuum systems because they are liquid and volatile. A very convenient absorbent may be made by suspending on 25–52 mesh powdered firebrick ('Eossalsil') 25 per cent by weight of a mull of sodium bisulphite in ethylene glycol. We have repeatedly used this powder packed in 10 cm. of a 15 mm. internal diameter tube to absorb the butyraldehyde remaining in a mixture after a photolysis. Subsequent analysis of the reaction products indicates that less than 0·3 μmole out of the initial 500 μmoles remains unabsorbed after the vapour has been passed three times through the packed tube. Acetone is not similarly absorbed.

An excellent absorbent for olefins may similarly be made from a mixture of 9 gm. mercuric acetate, 3 gm. mercuric nitrate and 20 gm. ethylene glycol on 100 gm. of firebrick.

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J. A. KERR
A. F. TROTMAN-DICKENSON
Chemistry Department,
The University,
Edinburgh 9.
June 12.

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THE REACTIONS OF ALKYL RADICALS

PART 1.—*n*-PROPYL RADICALS FROM THE PHOTOLYSIS OF *n*-BUTYRALDEHYDE

THE REACTIONS OF ALKYL RADICALS

PART 1.—*n*-PROPYL RADICALS FROM THE PHOTOLYSIS OF *n*-BUTYRALDEHYDE

By J. A. Kerr and A. F. Trotman-Dickenson
Chemistry Dept., The University, Edinburgh

Received 29th October, 1958

The photo-initiated chain decomposition of *n*-butyraldehyde, alone and when mixed with ethylene or propionaldehyde, has been studied. A mechanism that accounts for the rates of formation of the principal products has been constructed. On the assumption that the rate constant for the combination of *n*-propyl radicals is given by $\log k = 14$, the following Arrhenius parameters of the principal rate-determining reactions have been found:

	$\log A$	E
$2C_3H_7 = C_3H_6 + C_3H_8$	13·20	0
$C_3H_7 + C_3H_7CHO = C_3H_8 + C_3H_7CO$	11·3	6·7
$C_3H_7 + C_3H_7CHO = C_3H_8 + C_3H_6CHO$	11·3	10·8
$C_3H_7 = CH_3 + C_2H_4$	11·7	25·2
$C_3H_7 = H + C_3H_6$	13·6	35·0
$C_3H_7 + C_2H_4 = C_5H_{11}$	10·9	6·5

where k and A are in units of mole^{-1} cm^3 sec^{-1} or sec^{-1}, and E is in kcal mole^{-1}. The rate constant for the combination of ethyl and propyl is twice the geometric mean of the constants for the autocombinations.

The reactions of alkyl radicals containing more than two carbon atoms have been little investigated. There are two principal reasons for this neglect. First, the total analysis of the reaction products of a system in which propyl radicals, say, were major reactants has, until recently, been very difficult if not impossible. The invention of gas chromatography has now removed this impediment. The work described in this series of papers depends throughout on the chromatographic method of analysis.

The second reason has been the absence of suitable radical sources. The higher metallic alkyls are involatile and thermally unstable so that they cannot readily be used in photochemical systems. The temperatures and conditions of most thermal reaction systems are unsuitable for the study of many of the radical reactions that are of interest. This restriction arises directly from the limited temperature range over which the systems can be used. The mercury-photosensitized decomposition of paraffins and the photosensitized addition of hydrogen atoms to olefins have both been used as sources. They suffer from the disadvantage that the parent molecules are the same as the products of some of the more interesting reactions of the radicals. Their presence prevents the measurement of these products. A further disadvantage is that the systems are not sources of a single radical species, though usually the secondary and tertiary radicals are produced in preference to the primary. The photolyses of ketones are excellent sources of methyl and ethyl radicals. Unfortunately the photolysis of the higher ketones with α-hydrogen atoms does not cleanly yield the expected radicals. The quantum yields for the formation of other products are often high. Since the same products are produced by the reactions of the radicals themselves, their formation in the initial act considerably complicates the elucidation of the kinetics. Furthermore, those radicals that are formed are likely to carry over

significant amounts of excess energy from the initial act. Their chemical behaviour may not be the same as that of radicals in energetic equilibrium with their surroundings. The other radical sources discussed above may also yield excited radicals.

The photo-initiated chain decomposition of aldehydes has been little used as a source of radicals in the gas phase,[1] though it has been used in solution.[2] It has perhaps been disregarded because it is not a suitable source of radicals for the study of metathetical reactions unless heavily deuterated substrates are studied. This would make it possible to identify the products of the metatheses. The very high metathetical reactivity of the aldehydes makes it impossible to apply the treatment designed for ketonic sources.[3] The aldehydes are, however, good sources for most other purposes. The initial photolytic act is often not clean, but at higher temperatures the primary products are a very small proportion of the total, so they may generally be disregarded. When the chains are long the products formed by any excited radicals initially released may be disregarded for the same reason. Most of the alkyl radicals are formed by the thermal decomposition of the R . CO radicals.

The present paper is the record of a study of the reactions of the *n*-propyl radicals formed during the photo-initiated chain decomposition of *n*-butyraldehyde together with some experiments on the reactions occurring in mixtures with propionaldehyde and ethylene.

EXPERIMENTAL

MATERIALS

B.D.H. *n*-butyraldehyde was dried ($CaSO_4$) and fractionated. A constant-boiling fraction was distilled under vacuum and degassed. B.D.H. propionaldehyde was purified by bulb-to-bulb distillation with rejection of head and tail fractions. Samples of ethylene ethane and propane were obtained from B.O.G. cylinders. Propylene was prepared by dehydrating *iso*propanol.

APPARATUS

A cylindrical quartz reaction vessel (177 cm^3) which was connected to a conventional high-vacuum system was placed in a furnace kept to better than $\pm$ 1°C during a run. The cell was illuminated by the unfiltered light from a 125 W medium-pressure mercury arc. The intensity of illumination was varied by altering the position of the lamp.

The analytical system consisted of a low-temperature distillation train and a gas-chromatography unit. The products from the reaction vessel were first separated into non-condensables and condensables by a system of traps cooled in dry ice, liquid oxygen and liquid oxygen boiling under reduced pressure. The non-condensable hydrogen, methane and carbon monoxide were measured in a gas burette and then passed to a trap cooled in liquid oxygen containing activated silica gel. The uncondensed hydrogen was measured and pumped off. The silica gel was heated in hot water, the carbon monoxide burnt in a copper-oxide furnace as it came off and the carbon dioxide condensed with liquid oxygen. The methane was then measured.

The condensable fraction was passed through a short absorbent column to remove the aldehyde. The column was packed with 25-50 mesh powdered firebrick on which was suspended 25 % of a paste of sodium bisulphite in ethylene glycol.[4] If ethylene had been added to the reaction mixture it was similarly removed by a column of the firebrick mixed with a mercuric acetate + mercuric nitrate + ethylene glycol paste.[4] The gases that were not absorbed were passed into the chromatographic system which contained two types of column. Column A (300 $\times$ 0·5 cm) was packed with 25-52 mesh firebrick + 20 % dibutyl phthalate. Column B was packed with 30-52 mesh activated alumina impregnated with $\frac{1}{2}$ % squalane. The columns were operated at room temperature. A tap system was arranged so that after the lower-boiling materials through propylene had cleared columns A and B, the hexane could be taken directly from column A. The thermal-conducting-cell detector was coupled to a 0·5 mV recorder. Its sensitivity was determined for each hydrocarbon by passing known volumes of the gases through the columns. It was found that the olefins elicited the same response as the paraffins with the same carbon structure.

RESULTS AND DISCUSSION

The experimental results on the photolysis of pure *n*-butyraldehyde may be satisfactorily interpreted in terms of the following reaction scheme which takes account of work reported in the literature as well as the present investigation.

$$C_3H_7 . CHO + h\nu \begin{cases} = C_3H_7 + CHO & (a) \\ = C_3H_8 + CO & (b) \\ = C_2H_4 + CH_3 . CHO & (c) \\ = CH_3 + C_2H_4 + CHO & (d) \end{cases}$$

$$2C_3H_7 = C_6H_{14} \quad (1)$$

$$2C_3H_7 = C_3H_8 + C_3H_6 \quad (2)$$

$$C_3H_7 + C_3H_7 . CHO = C_3H_8 + C_3H_7 . CO \quad (3)$$

$$C_3H_7 . CO = C_3H_7 + CO \quad (3a)$$

$$C_3H_7 + C_3H_7 . CHO = C_3H_8 + C_3H_6 . CHO \quad (4)$$

$$C_3H_6 . CHO = C_3H_6 + HCO \quad (4a)$$

$$HCO + C_3H_7CHO = H_2CO + C_3H_7CO \quad (4b)$$

$$HCO = H + CO \quad (4c)$$

$$H + C_3H_7 . CHO = H_2 + C_3H_7 . CO \quad (4d)$$

$$C_3H_7 = CH_3 + C_2H_4 \quad (5)$$

$$CH_3 + C_3H_7 . CHO = CH_4 + C_3H_7 . CO \quad (5a)$$

$$2CH_3 = C_2H_6 \quad (5b)$$

$$C_3H_7 = H + C_3H_6 \quad (6)$$

THE PRIMARY PROCESS (*a*), (*b*), (*c*), (*d*)

Most of the available information on the nature of the primary process comes from the work of Leighton, Levanas, Blacet and Rowe,[5] and Blacet and Calvert.[6] They studied the photolysis both in the presence and absence of iodine with essentially monochromatic light of a variety of wavelengths. The work with iodine should give direct evidence on the relative importance of the different primary processes, but it is possible that the heavy atoms selectively de-activate the excited butyraldehyde molecules. Work on the photolysis of acetone in the presence of iodine is of interest in this connection.[7] Rather a high proportion of ethylene was found in the present work at low temperatures. This indicates that process (*c*) is important, accounting for perhaps 40 % of the quantum yield. Very little methane or ethane was found at low temperatures. (*d*) can therefore only account for 2 or 3 % of the quantum yield. (*a*) and (*b*) are probably of about equal importance as primary processes. These rather rough results correspond fairly well with those to be expected for light of about 2700 Å. This is a reasonable value for the mean effective wavelength of the photolytic light in the present experiments. Empirical corrections for the small amounts of methane released in the primary photolytic act have been applied where appropriate in the treatment of subsequent reactions.

THE COMBINATION OF *n*-PROPYL RADICALS (1) is the source of the *n*-hexane in the products formed according to the equation

$$R_{C_6H_{14}} = k_1[C_3H_7]^2.$$

Whiteway and Masson [8] attempted to measure k_1 by studying the photolysis of di-*n*-propyl ketone by the rotating-sector method. Extremely high values of k_1 were obtained. It is probable that the system is too complicated to be satisfactorily studied by the sector method, which gives results which are very susceptible to error if an inadequate mechanism is selected. In the present work it has been assumed throughout that

$$k_1/\text{mole}^{-1}\,\text{cm}^3\,\text{sec}^{-1} = 10^{14}.$$

It is quite likely that E_1, the activation energy of the reaction, is very low, but A_1 may differ by one or two powers of ten. A value is selected, although it is rather arbitrary, because it makes the presentation of the results more straightforward. When the true value of k_1 is discovered it will be a small matter to rescale the rate constants for the other reactions.

THE DISPROPORTIONATION OF *n*-PROPYL RADICALS (2).—Nine runs that provide direct information on k_2 were carried out between 25° and 191°C with mean aldehyde concentrations between 0·5 and 1·8 μmole cm^{-3}. The number of radicals

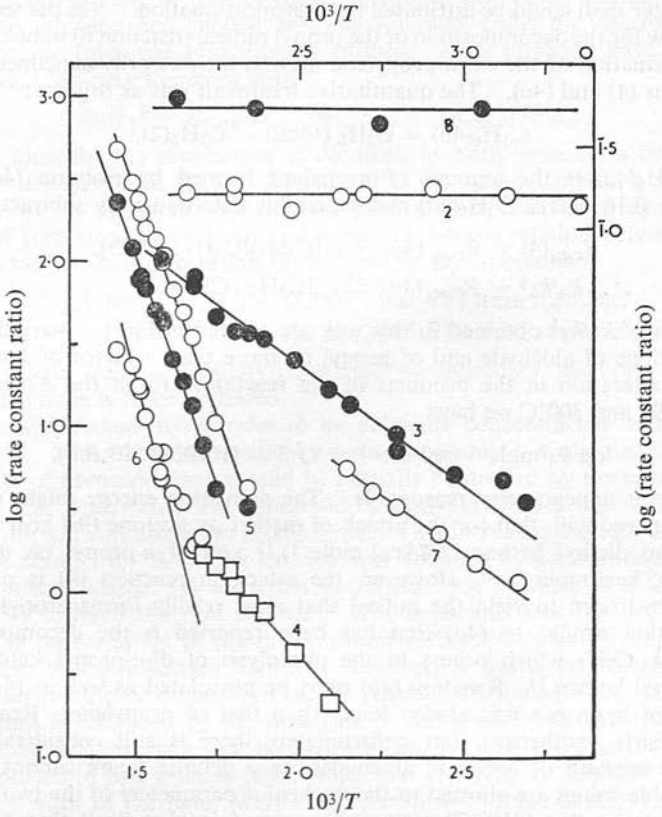

FIG. 1.—Arrhenius plots for the reactions of *n*-propyl: 2, disproportionation, k_2/k_1; 8, cross-combination, $k_8/(k_1k_9)^{\frac{1}{2}}$, the scales at the top right-hand corner refer to these plots; 3, hydrogen abstraction, $(k_3/k_1^{\frac{1}{2}})$/mole$^{-\frac{1}{2}}$ cm$^{3/2}$ sec$^{-\frac{1}{2}}$; 4, hydrogen abstraction, $(k_4/k_1^{\frac{1}{2}})$/mole$^{-\frac{1}{2}}$ cm$^{3/2}$ sec$^{-\frac{1}{2}}$; 5, decomposition to methyl and ethylene, $10^6(k_5/k_1^{\frac{1}{2}})$/mole$^{\frac{1}{2}}$ cm$^{-3/2}$ sec$^{-\frac{1}{2}}$, open circles, results based on methane, filled circles, results based on ethylene; 6, decomposition to propylene and a hydrogen atom, $10^6(k_6/k_1^{\frac{1}{2}})$/mole$^{\frac{1}{2}}$ cm$^{-3/2}$ sec$^{-\frac{1}{2}}$; 7, addition to ethylene, $(k_7/k_1^{\frac{1}{2}})$/mole$^{-\frac{1}{2}}$ cm$^{3/2}$ sec$^{-\frac{1}{2}}$.

disproportionating was taken as equal to twice the quantity of propylene found at the end of the run. Values of log (k_2/k_1) are plotted in fig. 1. $E_2 - E_1 = 0$, $A_2 = 0{\cdot}16\,A_1$. Therefore

$$\log k_2/\text{mole}^{-1}\,\text{cm}^3\,\text{sec}^{-1} = 13{\cdot}20.$$

Most previous workers have agreed that $E_2 - E_1 = 0$, but have obtained various values for A_2/A_1; for instance: 0·12 (Whiteway and Masson [8]), 0·1 (Blacet and Calvert [6]), 0·3 (Caule and Steacie [9]), 0·21 (Masson [10]). The result of Whiteway and Masson appears to be the most reliable and is in fair agreement with the

present work, though the difference would appear to be rather too great to be covered by the probable experimental errors. The lowest of the above results was obtained with mass-spectrometric analysis. It should be possible to determine small quantities of propylene in propane in this way. It may be noted, however, that the rate of disproportionation of *sec*-butyl radicals was seriously underestimated until gas chromatography was used.[1, 11]

THE ABSTRACTION OF HYDROGEN ATOMS FROM BUTYRALDEHYDE (4).—Above about 191°C the rate of production of propylene increased rapidly and became much greater than could be attributed to disproportionation. Yet the temperature was too low for the decomposition of the propyl radical (reaction 6) to be significant.

The formation of the extra propylene may be satisfactorily explained in terms of reactions (4) and (4*a*). The quantitative treatment was as follows:

$$C_3H_6(4a) = C_3H_6 \text{ (total)} - C_3H_6(2),$$

where $C_3H_6(4a)$ is the amount of propylene formed by reaction (4*a*). Since $C_3H_6(2) = 0{\cdot}16\ C_6H_{14}$, $C_3H_6(4a)$ may be readily determined by subtraction.

$$R_{C_3H_8}(4) = R_{C_3H_6}(4a) = k_4[C_3H_7][C_3H_7 \,.\, CHO].$$

$$\therefore\ k_4/k_1^{\frac{1}{2}} = R_{C_3H_6}(4a)/R_{C_6H_{14}}^{\frac{1}{2}}[C_3H_7 \,.\, CHO].$$

The values of $k_4/k_1^{\frac{1}{2}}$ obtained in this way are plotted in fig. 1. Variation of the concentrations of aldehyde and of propyl by more than a factor of 2 caused the predicted alteration in the products of the reaction. From the Arrhenius plot between 191 and 300°C we have

$$\log k_4/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1} = 11{\cdot}3 - (10800/2{\cdot}303\,RT).$$

The A factor appears very reasonable. The activation energy might seem high when compared with that for the attack of methyl on acetone (9·7 kcal mole^{-1}),[12] of ethyl on diethyl ketone (7·4 kcal mole^{-1}),[13] and of *n*-propyl on di-*n*-propyl ketone (6·5 kcal mole^{-1}).[10] However, the attack in reaction (4) is presumably on the β-hydrogen to yield the radical that most readily forms propylene. The only reaction similar to (4*a*) that has been reported is the decomposition of $C_3H_6 \,.\, CO \,.\, C_3H_7$ which occurs in the photolysis of di-*n*-propyl ketone [10] and di-*iso*-propyl ketone.[14] Reaction (4*b*) must be postulated as well as (4*c*) because the yield of hydrogen was always lower than that of propylene. Reaction (4*b*) may be fairly exothermic, but unfortunately there is still considerable doubt about the strength of bonds in aldehydes, so a definite figure cannot be given. If reasonable values are allotted to the Arrhenius parameters of the two reactions, it can be shown that (4*b*) will account for more formyl radicals than (4*c*).

THE ABSTRACTION OF HYDROGEN ATOMS FROM BUTYRALDEHYDE (3).—It would be expected that the aldehydic hydrogen would be much the more reactive hydrogen atom in butyraldehyde because acetaldehyde is much more reactive towards methyl than is the majority of compounds.[15] Furthermore, Birrell and Trotman-Dickenson [16] have shown that the butyraldehydes react with methyl at almost exactly the same rate as do acetaldehyde and propionaldehyde. In this work, the rate of attack of propyl on butyraldehyde has been taken to be equal to

$$R_{C_3H_8} - R_{C_3H_6}(4a) - R_{C_3H_6}(2),$$

as is required by the mechanism. At low temperatures this is effectively

$$R_{C_3H_8} - R_{C_3H_6}.$$

Hence we may write

$$k_3/k_1^{\frac{1}{2}} = (R_{C_3H_8} - R_{C_3H_6})/R_{C_6H_{14}}^{\frac{1}{2}}[C_3H_7 \,.\, CHO].$$

In this expression as in the analogous one for reaction (4) $[C_3H_7 \,.\, CHO]$ refers to the mean concentration of the aldehyde. In extreme cases, 40 % of the alde-

hyde was consumed. The Arrhenius plot shown in fig. 1 for results obtained between 98 and 361°C yields

$$\log k_3/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1} = 11{\cdot}3 - (6700/2{\cdot}303\,RT).$$

Measurements [6] of the temperature coefficient of the quantum yield for carbon monoxide formation in the photolysis of *n*-butyraldehyde suggested [17] that $E_3 - \frac{1}{2}E_1 = 5{\cdot}6$ kcal mole^{-1}. The original authors did not stress this tentative interpretation. It is not surprising that the present work yields a higher value.

THE DECOMPOSITION OF *n*-PROPYL TO ETHYLENE (5).—The decomposition of *n*-propyl to ethylene and methyl may be followed either by determining the ethylene or the (methane plus ethane) formed. Both methods have been employed here. We may therefore write

$$k_5/k_1^{\frac{1}{2}} = R_{C_2H_4}/R_{C_6H_{14}}^{\frac{1}{2}} = (R_{CH_4} + 2R_{C_2H_6})/R_{C_6H_{14}}^{\frac{1}{2}}.$$

Arrhenius plots for the rate constants obtained by both procedures between 270 and 421°C are shown in fig. 1. Above 313°C the hexane formed a very small proportion of the products. Its amount was therefore determined by measuring the rate of formation of propane and using the known relation between k_1 and k_3. The rate constant of reaction (5) is given by the expression:

$$\log k_5/\text{sec}^{-1} = 11{\cdot}7 - (25200/2{\cdot}303\,RT) \text{ from methane,}$$
$$\log k_5/\text{sec}^{-1} = 11{\cdot}4 - (25300/2{\cdot}303\,RT) \text{ from ethylene.}$$

As the ethylene may be partially consumed by secondary reactions, the value based on methane is to be preferred.

The results quoted above refer to an aldehyde concentration of about 0·58 μmole cm^{-3}. Since the propyl radical is a small molecule it is reasonable to expect that its rate of decomposition should be partially controlled by the rate of energy transfer. This dependence was confirmed by studying the decomposition in three times the normal concentration of aldehyde. This increased the rate constant by a factor of about 1·6. A similar increase was obtained by adding some 15 μmole cm^{-3} of carbon dioxide. A reduction in the aldehyde pressure by a factor of 20 considerably lowered the rate constant. The apparatus was not well suited to the study of the variation of the rate constant with pressure so this aspect of the investigation was not carried further. However, it seems very likely that the low *A* factor for the decomposition can be partially attributed to the fact that the rate constant is restricted by the slow rate of energization of the radicals. The high-pressure *A* factor may well be over 10^{12} sec^{-1}. The value of the activation energy reported in this work is higher than that reported by Masson [10] or in the preliminary work of Durham, Martin and Sutton.[18] These authors did not give sufficient information in their publications to make possible a comparison of the rates.

THE DECOMPOSITION OF *n*-PROPYL TO PROPYLENE (6).—Above 300°C the rate of production of propylene begins to rise sharply. This increase can be attributed to the decomposition of the propyl radical, so we can write

$$k_6/k_2^{\frac{1}{2}} = (R_{C_3H_6} - R_{C_3H_6}(4) - R_{C_3H_6}(2))/R_{C_6H_{14}}^{\frac{1}{2}}.$$

Again it is necessary to calculate the rate of formation of the hexane from that for propane. The results obtained between 347 and 421°C are plotted in fig. 1. Above 420°C, *n*-butyraldehyde decomposes inconveniently rapidly so that the range over which results were obtained is restricted. The need to correct for the formation of propylene by two additional reactions does not introduce unreasonable errors as can be seen from fig. 2 which shows the amount of propylene attributed to each reaction over the range of temperatures. Nevertheless, definite Arrhenius parameters cannot be found. The most that can be said is that the results are consistent with

$$\log k_6/\text{sec}^{-1} = 13{\cdot}6 - (35000/2{\cdot}303\,RT)$$

which corresponds to the line drawn in fig. 1. From the preliminary results it appeared that k_6 was rather less dependent on pressure than k_5.

THE ADDITION OF *n*-PROPYL TO ETHYLENE (7).—When ethylene is added to the *n*-butyraldehyde, reaction (7) takes place,

$$C_3H_7 + C_2H_4 = C_5H_{11}. \qquad (7)$$

This is followed by

$$C_5H_{11} + C_3H_7 . CHO = C_5H_{12} + C_3H_7 . CO, \qquad (7a)$$

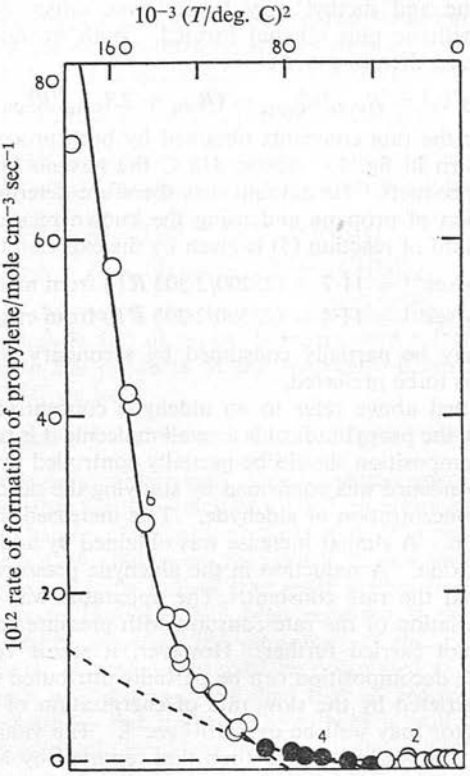

FIG. 2.—The rate of formation of propylene by disproportionation (2), decomposition of C_3H_6CO (4), and decomposition of C_3H_7 (6), showing the relative importance of the sources at different temperatures.

which accounts for about 80 % of the pentyl radicals if the concentration of the ethylene is double that of the aldehyde. About 10 % of the pentyl radicals add a further molecule of ethylene (7*b*),

$$C_5H_{11} + C_2H_4 = C_7H_{15}, \qquad (7b)$$

which reacts to give heptane. A proportional correction is then made to allow for the 1 % of the initial radicals which ultimately form nonane. The remaining pentyl radicals dimerize, combine with propyl and disproportionate. The quantities of these products were small and no attempt was made to determine them. Their amount was estimated on the assumption that *n*-pentyl radicals react like *n*-propyl radicals. An error of 10 % in this estimate leads to an error of only 1 % in k_7. Hence we can write

$$k_7/k_1^{\frac{1}{2}} = R_{\text{pentyl products}}/R_{C_6H_{14}}^{\frac{1}{2}}[C_2H_4].$$

It may be noted that it is particularly convenient to study the addition of a radical with an odd number of carbon atoms to ethylene in this way, for the determination is simply based on the measurement of *n*-pentane, *n*-hexane and *n*-heptane.

The rate constant k_7 is given by

$$\log k_7/\text{mole}^{-1}\,\text{cm}^3\,\text{sec}^{-1} = 10{\cdot}9 - (6500/2{\cdot}30\,RT).$$

No previous work on the addition of *n*-propyl to simple olefins has previously been reported. Szwarc [19] has compared the rates at which alkyl radicals add to polynuclear aromatic hydrocarbons (k_a) with the rate at which they abstract hydrogen atoms from *iso*-octane (k_b). He found that for a given hydrocarbon k_a/k_b was about seven times as great for *n*-propyl radicals as for methyl radicals at 65°C. We may compare

$$\frac{k\ (\text{addition of radical to ethylene})}{k\ (\text{abstraction of H atom from butyraldehyde})} = \frac{k_a'}{k_b'}$$

for methyl and *n*-propyl radicals at 143°C. It is found that k_a'/k_b' is twice as great for methyl [16, 20, 21] as for *n*-propyl radicals. It does not seem likely that the change in medium can be solely responsible for this reversal of reactivities.

THE COMBINATION OF ETHYL AND *n*-PROPYL (8).—When a mixture of propionaldehyde and *n*-butyraldehyde is photolyzed, pentane and butane are among the products. They are presumably formed by reactions (8) and (9):

$$C_2H_5 + C_3H_7 = C_5H_{12}, \qquad (8)$$

$$2C_2H_5 = C_4H_{10}. \qquad (9)$$

Hence $$k_8/(k_1k_9)^{\frac{1}{2}} = R_{C_5H_{12}}/(R_{C_4H_{10}}R_{C_6H_{14}})^{\frac{1}{2}}.$$

The results, plotted in fig. 1, show that between 54 and 198°C,

$$k_8/(k_1k_9)^{\frac{1}{2}} = 1{\cdot}9 \pm 0{\cdot}2$$

and is independent of temperature within the rather large experimental error. This ratio of rate constants has not been previously determined though McNesby and Gordon [22] have found that the comparable ratio for *n*-propyl with methyl is 2·6 at 150°C. Evidently the cross-combination of alkyl radicals is favoured over the combination of like radicals but not to the same degree as is frequently found for terminations in copolymerizations, when the reacting radicals are more polar. The ratios are close to the value of two predicted by the simple collision theory.

THE ENERGETICS OF RADICAL DECOMPOSITIONS

The following relations govern the energetics of the decomposition of *n*-propyl radicals to methyl and ethylene:

$$D(CH_3{-}CH_2CH_2{-}) = \Delta H_f^\circ(CH_3) + \Delta H_f^\circ(C_2H_4) - \Delta H_f^\circ(n\text{-}C_3H_7)$$
$$= E_5 - E_{-5}.$$

But $$\Delta H_f^\circ(n\text{-}C_3H_7) = \Delta H_f^\circ(C_3H_8) + D(C_3H_7{-}H) - \Delta H_f^\circ(H).$$

$$\therefore E_5 - E_{-5} = \Delta H_f^\circ(CH_3) + \Delta H_f^\circ(C_2H_4) - \Delta H_f^\circ(C_3H_8) - D(C_3H_7{-}H) + \Delta H_f^\circ(H).$$

Substituting we have

$$25{\cdot}2 - E_{-5} = 32{\cdot}5 + 12{\cdot}5 + 24{\cdot}8 - D(C_3H_7{-}H) + 52,$$

$$\therefore D(C_3H_7{-}H) = E_{-5} + 96{\cdot}6.$$

The results obtained in this work and those in the literature [23, 24] indicate that E_{-5} is very unlikely to be less than 6 kcal mole^{-1}. Hence

$$D(C_3H_7{-}H) \geqslant 102{\cdot}6 \text{ kcal mole}^{-1}.$$

A similar calculation may be carried out for the decomposition of *n*-propyl into propylene and a hydrogen atom. From which it may be shown that

$$D(C_3H_7—H) \geqslant 104{\cdot}1 \text{ kcal mole}^{-1},$$

if the activation energy for the addition of a hydrogen atom to propylene at the central carbon atom has 5 kcal mole^{-1} of activation energy. Although the two determinations are in as good agreement as could be expected, little reliance should be placed on the second determination because the activation energy on which it is based was not properly determined. The calculated dissociation energy is considerably higher than would have been expected. It would be lowered if E_5 had been underestimated or if $\frac{1}{2}E_1$ is greater than zero. It does not seem likely that either value can be sufficiently in error to reduce $D(C_3H_7—H)$ from equality with $D(CH_3—H)$ to equality with $D(C_2H_5—H)$ or about 98 kcal mole^{-1}. The high value for $D(C_3H_7—H)$ which has previously been reported on the basis of totally different determinations [25, 26] is strongly supported by the present work.

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THE REACTIONS OF ALKYL RADICALS

PART 2.—*S*-PROPYL RADICALS FROM THE PHOTOLYSIS OF *ISO*BUTYRALDEHYDE

BY J. A. KERR AND A. F. TROTMAN-DICKENSON
Chemistry Dept., The University, Edinburgh

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The photo-initiated chain decomposition of *iso*butyraldehyde, alone and when mixed with ethylene or propionaldehyde, has been studied. A mechanism that accounts for the rates of formation of the principal products has been constructed. The amounts of hydrogen, carbon monoxide, methane, ethylene, propane, propylene and 2 : 3-dimethyl butane were determined in the runs with the pure aldehyde. On the basis of an assumed rate constant for the combination of *s*-propyl radicals, activation energies and *A* factors for disproportionation, hydrogen abstraction, addition to ethylene, and decomposition both to ethylene and propylene were obtained. The results are summarized and compared with similar results for *n*-propyl in table 1. The rate constant for the combination of ethyl and *s*-propyl is twice the geometric mean of the constants for the autocombinations.

The first paper in this series [1] described the reactions of *n*-propyl radicals produced in the photoinitiated chain decomposition of *n*-butyraldehyde. This paper deals with a parallel study of *s*-propyl radicals from *iso*butyraldehyde. More was previously known of these radicals because they can be cleanly produced by the photolysis of di-*iso*propyl ketone. They are also principally formed in the mercury-photosensitized addition of hydrogen to propylene and in the mercury-photosensitized decomposition of propane.

EXPERIMENTAL

The apparatus, the procedure, and many of the gases were the same as were employed in part 1. B.D.H. *iso*butyraldehyde was degassed before use. Gas chromatographic analysis showed it to be pure.

RESULTS AND DISCUSSION

Twenty-five runs were carried out in which the photo-initiated chain decomposition of *iso*butyraldehyde was studied between 20° and 501°C. The products were analyzed for carbon monoxide, hydrogen, methane, ethylene, propylene, propane and 2 : 3-dimethyl butane. No ethane was detected. The results, taken in conjunction with other work referred to later, indicate that all the following reactions take place to a measurable extent, though others cannot be definitely excluded.

$$(CH_3)_2CHCHO + h\nu \rightarrow C_3H_7 + CHO \quad (a)$$
$$\rightarrow C_3H_8 + CO \quad (b)$$
$$\rightarrow CH_3 + C_2H_4CHO \quad (c)$$
$$2C_3H_7 = C_6H_{14} \quad (1)$$
$$2C_3H_7 = C_3H_6 + C_3H_8 \quad (2)$$
$$C_3H_7 + C_3H_7CHO = C_3H_8 + C_3H_7CO \quad (3)$$
$$(CH_3)_2CHCO = (CH_3)_2CH + CO \quad (3a)$$

$$C_3H_7 + (CH_3)_2CHCHO = C_3H_8 + CH_2(CH_3)CHCHO \quad (4)$$
$$CH_2(CH_3)CHCHO = C_3H_6 + HCO \quad (4a)$$
$$HCO = H + CO \quad (4b)$$
$$H + C_3H_7CHO = H_2 + C_4H_7O \quad (4c)$$
$$HCO + C_3H_7CHO = H_2CO + C_4H_7O \quad (4d)$$
$$C_3H_7 + (CH_3)_2CHCHO = C_3H_8 + (CH_3)_2CCHO \quad (5)$$
$$(CH_3)_2CCHO = C_2H_3CHO + CH_3 \quad (5a)$$
$$CH_3 + C_3H_7CHO = CH_4 + C_4H_7O \quad (5b)$$
$$(CH_3)_2CCHO \rightarrow \text{unidentified products} \quad (5c)$$
$$C_3H_7 = CH_3 + C_2H_4 \quad (6)$$
$$C_3H_7 = H + C_3H_6. \quad (7)$$

THE PHOTOLYTIC ACT (*a*), (*b*), (*c*)

The most complete evidence on the nature of the photolytic act comes from the work of Blacet and Calvert.[2] They studied the products of the photolysis of the pure substance and in mixtures with iodine. With radiation of 2654 Å, approximately equal numbers of molecules react by (*a*) and (*b*), but only one-tenth the number react by (*c*). In the present work, very small quantities of methane were produced at low temperatures. Even below 60°C, considerable quantities of propane were evidently formed by the chain process. The majority of the radicals present must then have been formed by (3*a*) and have been in energetic equilibrium with their environment. At 410°C the quantum yield for the formation of carbon monoxide was at least twenty times its value at 20°C.

THE COMBINATION OF *s*-PROPYL (1)

No measurements of the rate of combination of *s*-propyl have been reported although it would seem easier to investigate the photolysis of di-*iso*propyl ketone than di-*n*-propyl ketone by the rotating sector method. In the absence of any experimental determination, a conventional rate constant,

$$\log k_1/\text{mole}^{-1}\,\text{cm}^3\,\text{sec}^{-1} = 14,$$

has been assumed for the purposes of presenting the results. E_1 has been taken as zero because it is convenient. It is likely that this activation energy may be 1-2 kcal mole^{-1}, but not more.

THE DISPROPORTIONATION OF *s*-PROPYL (2)

One molecule of propylene is formed for each pair of propyl radicals that disproportionate. At low temperatures propylene is apparently only formed in this way, therefore

$$k_2 = R_{C_3H_6}/[C_3H_7]^2,$$

where $R_{C_3H_6}$ is the rate of formation of propylene. But

$$k_1 = R_{C_6H_{14}}/[C_3H_7]^2.$$

Therefore

$$k_2/k_1 = R_{C_3H_6}/R_{C_6H_{14}}.$$

The values that have been obtained in this way between 20° and 261°C are plotted in fig. 1. The line may be represented by the equation,

$$\log k_2/\text{mole}^{-1}\,\text{cm}^3\,\text{sec}^{-1} = 13{\cdot}82.$$

This rate constant corresponds to a value of $k_2/k_1 = 0{\cdot}65$ that is independent of temperature and was found not to vary when the aldehyde concentration was altered by a factor of five and the intensity of the absorbed light by about the

same ratio. The result is in excellent agreement with that (0·63) of Heller and Gordon [3] from the photolysis of di-*iso*propyl ketone. The agreement is less good with the earlier work of Blacet and Calvert [2] (0·5) and Durham and Steacie [4] (0·53 at 30°C; 0·36 at 121°C) who used the photolysis of *iso*butyraldehyde and azo*iso*propane respectively as sources. The rather less accurate result (approx. 0·6) that Chilton and Gowenlock [5] obtained from a study of the pyrolysis of di-*iso*propyl mercury between 225° and 441°C is in as good agreement as could be expected. On the other hand Bradley, Melville and Robb [6] found that *s*-propyl radicals produced in 92 % purity by the mercury photosensitized addition of hydrogen atoms to propylene yielded a disproportionation ratio of 1·05 at 25°C. The radicals may have contained appreciable excess energy because of their method of formation. At the moment it would seem that the lower values should be preferred.

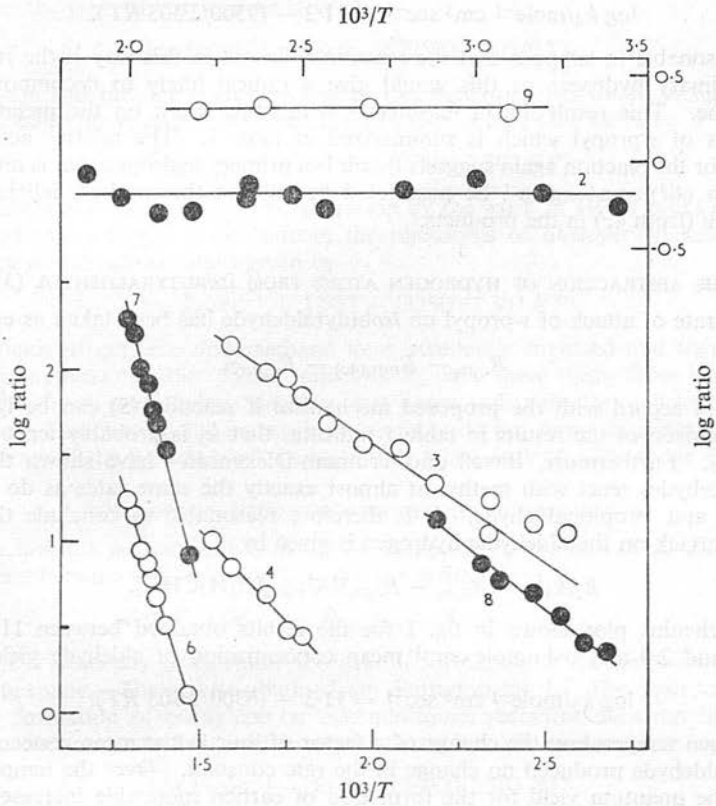

FIG. 1.—Arrhenius plots for the reactions of *s*-propyl: 2, disproportionation, k_2/k_1; 9, cross-combination, $k_9/(k_1k_{10})^{\frac{1}{2}}$, the scales at the top right-hand corner refer to these plots; 3, hydrogen abstraction, $(k_3/k_1^{\frac{1}{2}})$/mole$^{-\frac{1}{2}}$ cm$^{3/2}$ sec$^{-\frac{1}{2}}$; 4, hydrogen abstraction, $(k_4/k_1^{\frac{1}{2}})$/mole$^{-\frac{1}{2}}$ cm$^{3/2}$ sec$^{-\frac{1}{2}}$; 6, decomposition to methyl and ethylene, $10^6(k_6/k_1^{\frac{1}{2}})$/mole$^{\frac{1}{2}}$ cm$^{-3/2}$ sec$^{-\frac{1}{2}}$; 7, decomposition to propylene and a hydrogen atom, $10^6(k_7/k_1^{\frac{1}{2}})$/mole$^{\frac{1}{2}}$ cm$^{-3/2}$ sec$^{-\frac{1}{2}}$; 8, addition to ethylene, $(k_8/k_1^{\frac{1}{2}})$/mole$^{-\frac{1}{2}}$ cm$^{3/2}$ sec$^{-\frac{1}{2}}$.

THE ABSTRACTION OF HYDROGEN ATOMS FROM *iso*BUTYRALDEHYDE (4)

Above about 280°C the rate of production of propylene began to increase rapidly and in a way that could not be explained by disproportionation or by the decomposition of the *s*-propyl radical (reaction (7)). Reactions (4) and (4*a*) appear to account satisfactorily for the propylene in this photolysis; similar

reactions were invoked in the discussion of the photolysis of *n*-butyraldehyde. We may write

$$C_3H_6\,(4a) = C_3H_6\,(\text{total}) - C_3H_6\,(2),$$

where $C_3H_6\,(4a)$ is the amount of propylene formed by reaction (4*a*). Since $C_3H_6\,(2) = 0{\cdot}65\ C_6H_{14}$, $C_3H_6\,(4a)$ may be found by subtraction. Then

$$R_{C_3H_8(4)} = R_{C_3H_6(4a)} = k_4[C_3H_7][C_3H_7CHO],$$

$$\therefore\ k_4/k_1^{\frac{1}{2}} = R_{C_3H_6(4a)}/R^{\frac{1}{2}}_{C_6H_{14}}[C_3H_7CHO].$$

The values of $k_4/k_1^{\frac{1}{2}}$ obtained in this way are plotted in fig. 1. From the Arrhenius plot between 283° and 377°C and for aldehyde concentrations between 0·52 and 1·20 μmole cm^{-3} we have

$$\log k_4/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1} = 11{\cdot}2 - (9500/2{\cdot}303\ RT).$$

It is reasonable to suppose that the reaction followed in this way is the removal of a primary hydrogen as this would give a radical likely to decompose into propylene. This result fits in reasonably with other work on the metathetical reactions of *s*-propyl which is summarized in table 1. The relative activation energy for the reaction again suggests that it is a primary hydrogen that is removed. Reaction (4*d*) must again [1] be postulated because of the marked deficiency of hydrogen (from 4*c*) in the products.

THE ABSTRACTION OF HYDROGEN ATOMS FROM *iso*BUTYRALDEHYDE (3)

The rate of attack of *s*-propyl on *iso*butyraldehyde has been taken as equal to

$$R_{C_3H_8} - R_{C_3H_6(4a)} - R_{C_3H_6(2)}.$$

This is in accord with the proposed mechanism if reaction (5) can be ignored. A comparison of the results in table 1 indicates that k_3 is probably ten or more times k_5. Furthermore, Birrell and Trotman-Dickenson [7] have shown that the butyraldehydes react with methyl at almost exactly the same rates as do acetaldehyde and propionaldehyde. It is therefore reasonable to conclude that the rate of attack on the aldehydic hydrogen is given by

$$k_3/k_1^{\frac{1}{2}} = (R_{C_3H_8} - R_{C_3H_6})/R^{\frac{1}{2}}_{C_6H_{14}}[C_3H_7CHO].$$

The Arrhenius plot shown in fig. 1 for the results obtained between 117° and 354°C and 2·0 and 0·4 μmole cm^{-3} mean concentration of aldehyde yields

$$\log k_3/\text{mole}^{-1}\ \text{cm}^3\ \text{sec}^{-1} = 11{\cdot}3 - (6300/2{\cdot}303\ RT).$$

At a given temperature the change of a factor of four in the mean concentration of the aldehyde produced no change in the rate constant. Over the temperature range the quantum yield for the formation of carbon monoxide increased by a factor of approximately twelve.

Reaction (5) may be conveniently considered after reaction (6).

THE DECOMPOSITION OF *s*-PROPYL TO ETHYLENE (6)

When this work was begun it was thought that reaction (6) would not occur as information in the literature indicated that the parallel reactions of *s*-butyl are very slow.[8] It was found, however, that above 400°C considerable quantities of ethylene were formed and that the small amount of methane, that was produced at low temperatures, increased rapidly. These findings could be simply explained only if the *s*-propyl radical decomposed to methyl and ethylene. We may therefore write:

$$k_6/k_1^{\frac{1}{2}} = R_{C_2H_4}/R^{\frac{1}{2}}_{C_6H_{14}} = R_{CH_4}/R^{\frac{1}{2}}_{C_6H_{14}}.$$

The amounts of hexane were so small that they were estimated from measurements of $R_{C_3H_8}$ and the known relation between k_1, k_3 and k_4. Unfortunately, the rate of formation of methane, though rather irreproducible, is consistently about three times the rate of formation of ethylene. This discrepancy is too great to be attributed to the consumption of ethylene.

It is possible that the additional methyl leading to methane (reaction (5*b*)) is released by the decomposition of the aldehydic radical (5*a*). Since the ratio of $k_3 : k_4 : k_5$ will probably vary little between 400° and 500°C, the concentration of $(CH_3)_2CCHO$ could be proportional to the concentration of propyl. Furthermore since (5*a*) which yields acrolein is analogous to (6) it is likely that their activation energies are similar. The reaction sequence (5) may therefore be regarded as a reasonable explanation of the findings although there is little direct evidence for it. No useful estimate of k_5 can be made.

From the yield of ethylene we have

$$\log k_6/\text{sec}^{-1} = 10{\cdot}6 - (29500/2{\cdot}303\,RT).$$

The points and the line corresponding to this equation are plotted in fig. 1. If the rate constant is calculated from the methane production we have

$$\log k_6/\text{sec}^{-1} = 10{\cdot}3 - (27100/2{\cdot}303\,RT).$$

Some doubt is thrown on this interpretation by the work of Heller and Gordon [9] who find that *s*-propyl radicals from the photolysis of di-*iso*propyl ketone decompose with a rate constant given by

$$\log k_6/\text{sec}^{-1} = 12{\cdot}03 - (32500/2{\cdot}303\,RT).$$

Their yields of ethylene and methane were excellently matched and their determination appears reliable. Their values of k_6 were three times those derived in this work from the ethylene analyses but agree well with those based on the methane. Fortunately, the uncertainties as to k_6 do not seriously affect the other conclusions of the present work because they relate only to runs above 400°C.

THE DECOMPOSITION OF *s*-PROPYL TO PROPYLENE (7)

Reaction (7) satisfactorily explains the steep rise in the rate of production of propylene between 400° and 500°C. We can write

$$k_7/k_1^{\frac{1}{2}} = (R_{C_3H_6} - R_{C_3H_6(4a)} - R_{C_3H_6(2)})/R^{\frac{1}{2}}_{C_6H_{14}}.$$

Again it is necessary to calculate the rate of formation of the hexane from that of the propane. The results obtained are plotted in fig. 1. The need to correct for the formation of propylene by two additional reactions does not introduce unreasonable errors as their contributions are small. The rate constant is given by

$$\log k_7/\text{sec}^{-1} = 13{\cdot}8 - (36900/2{\cdot}303\,RT).$$

These rate constants are in excellent agreement with those of Heller and Gordon [9] given by

$$\log k_7/\text{sec}^{-1} = 13{\cdot}1 - (35000/2{\cdot}303\,RT).$$

The Arrhenius parameters agree within the probable experimental errors.

Bywater and Steacie [10] measured k_6 and k_7 for the propyl radicals produced by the mercury-photosensitized decomposition of propane. At 440°C, about one-third of the steady-state concentration of propyl radicals were formed by the removal of a primary hydrogen atom from propane. The rate constants that can be derived from their results are given by [11]

$$\log k_6'/\text{sec}^{-1} = 9{\cdot}2 - (20000/2{\cdot}303\,RT)$$

and

$$\log k_7'/\text{sec}^{-1} = 14{\cdot}6 - (38000/2{\cdot}303\,RT).$$

The logarithms of their rate constants at 440°C ($\log k_6' = 3{\cdot}1$, $\log k_7' = 3{\cdot}0$) are reasonably in accord with those of Heller and Gordon for *s*-propyl ($\log k_6 = 2{\cdot}0$, $\log k_7 = 2{\cdot}5$) and ours for *s*-propyl ($\log k_6 = 1{\cdot}5$, $\log k_7 = 2{\cdot}5$) and for *n*-propyl [1] ($\log k_6^* = 4{\cdot}0$, $\log k_7^* = 2{\cdot}9$). It seems that most of Steacie and Bywater's products were formed by the decomposition of the *n*-propyl radicals.

The effect of the total pressure on the rate constants was not investigated.

THE ADDITION OF *s*-PROPYL TO ETHYLENE (8)

When ethylene is added to the *iso*butyraldehyde, reaction (8) takes place:

$$C_3H_7 + C_2H_4 = C_5H_{11}. \qquad (8)$$

It is followed by

$$C_5H_{11} + C_3H_7CHO = C_5H_{12} + C_4H_7O, \qquad (8a)$$

which accounts for about 85 % of the *iso*pentyl radicals if the concentration of the ethylene is double that of the aldehyde. About 10 % of the *iso*pentyl radicals add a further molecule of ethylene (8*b*)

$$C_5H_{11} + C_2H_4 = C_7H_{15} \qquad (8b)$$

and subsequently form 2-methyl hexane. A proportional correction of 1 % was made to allow for the *iso*pentyl radicals that ultimately form 2-methyl octane. The remaining *iso*pentyl radicals presumably dimerize, combine with propyl and disproportionate. The quantities of these products were small and no attempt was made to analyse for them. Their amount was estimated by making the assumption that *iso*pentyl radicals react like *s*-propyl radicals. An error of 10 % in this estimate probably leads to an error of only 1 % in k_8. Hence we can write

$$k_8/k_1^{\frac{1}{2}} = R\,(\text{pentyl products})/R^{\frac{1}{2}}_{C_6H_{14}}[C_2H_4].$$

The results obtained in this way are plotted in fig. 1. Hence

$$\log k_8/\text{mole}^{-1}\,\text{cm}^3\,\text{sec}^{-1} = 11{\cdot}4 - (6900/2{\cdot}303\,RT).$$

The Arrhenius parameters are very close to those for the similar reaction of *n*-propyl, given in table 1, but are lower than those for the addition of methyl to ethylene,[12]

$$\log k/\text{mole}^{-1}\,\text{cm}^3\,\text{sec}^{-1} = 12{\cdot}0 - (8660/2{\cdot}303\,RT).$$

THE COMBINATION OF ETHYL AND *s*-PROPYL (9)

When a mixture of propionaldehyde and *iso*butyraldehyde is photolysed *iso*pentane and *n*-butane are among the products. They are presumably formed by reactions (9) and (10),

$$C_2H_5 + C_3H_7 = C_5H_{12} \qquad (9)$$

$$2C_2H_5 = C_4H_{10}. \qquad (10)$$

Hence $$k_9/(k_1k_{10})^{\frac{1}{2}} = R_{C_5H_{12}}/(R_{C_4H_{10}}R_{C_6H_{14}})^{\frac{1}{2}}.$$

The results plotted in fig. 1 show that between 50° and 200°C, $k_9/(k_1k_{10})^{\frac{1}{2}} = 2{\cdot}04$ and is independent of temperature. A similar ratio may be derived from Wijnen's[13] determinations of the products formed in the photolysis of *iso*propyl propionate.[14]

THE ENERGETICS OF THE DECOMPOSITION OF *s*-PROPYL

The best available values of the Arrhenius parameters for the reactions of propyl radicals are listed in table 1. The most remarkable feature of the table is the similarity of the activation energies of the reactions of *n*- and *s*-propyl, for

TABLE 1.—THE REACTIONS OF PROPYL RADICALS

n-propyl reaction	log *A*	*E*	ref.	*s*-propyl reaction	log *A*	*E*	ref.
COMBINATION	14·0	0	*a*		14·0	0	*a*
DISPROPORTIONATION	13·2	0	1		13·82	0	*b*
H-TRANSFER REACTIONS							
n-$C_3H_7C\underline{H}O$	11·3	6·7	1	*iso*$C_3H_7CO\underline{H}$	11·3	6·3	*b*
n-$C_3\underline{H}_7CHO$	11·3	10·8	1	$(C\underline{H}_3)_2CHCHO$	11·2	9·5	*b*
$(n$-$C_3\underline{H}_7)_2CO$	10·7	6·5	*c*	$((C\underline{H}_3)_2C\underline{D})_2CO$	11·1	9·3	9
				$((C\underline{H}_3)_2C\underline{D})_2CO$	11·8	11·7	9
				$((C\underline{H}_3)_2C\underline{H}N)_2$	10·4	6·5	4
DECOMPOSITION REACTIONS							
loss of CH_3	11·7	25·2	1	loss of CH_3	12·0	32·5	9
loss of H	13·6	35·0	1	loss of H	13·8	36·9	*b*
ADDITION REACTIONS							
to ethylene	10·9	6·5	1	to ethylene	11·4	6·9	*b*

All *A* factors are in mole^{-1} cm^3 sec^{-1} or sec^{-1}; *E* in kcal mole^{-1}.

(*a*) These values are assumed and are the basis of all the other rate constants.
(*b*) this work.
(*c*) Masson, *J. Amer. Chem. Soc.*, 1952, **74**, 4731.
The atoms underlined are those attacked in the transfer reactions.

it is generally believed that the strengths of the bonds broken when the radicals are formed from propane differ by three or more kcal mole^{-1}. The activation energies for the decompositions are most informative about the strengths of the bonds. In part 1 it was shown from simple thermodynamic arguments that

$$D(n\text{-}C_3H_7\text{—}H) = E^*_{-6} + 96{\cdot}6 \text{ and } E^*_{-7} + 99{\cdot}1,$$

where E^*_6 and E^*_7 are the activation energies for the decompositions of *n*-propyl into ethylene and propylene respectively (the negative sign denotes the reverse reaction throughout). In the same way it can be shown that

$$D(s\text{-}C_3H_7\text{—}H) = E_{-6} + 89{\cdot}3 \text{ and } E_{-7} + 96{\cdot}8.$$

The incomplete evidence presently available indicates that the activation energies for the addition of hydrogen atoms and methyl radicals do not differ by more than 1 or 2 kcal mole^{-1}. Hence there is a discrepancy between the determinations of E_6 and E_7 of about 7 kcal mole^{-1}.

The value of $D(s\text{-}C_3H_7\text{—}H)$ that is currently accepted as the most probable is 94 kcal mole^{-1}. If E_{-6} is allotted the reasonable value of 8 kcal mole^{-1}, we have $D(s\text{-}C_3H_7\text{—}H) = 89{\cdot}3 + 8 = 97$ kcal mole^{-1} from the kinetic measurements. This value is, within the limits of the accumulated experimental errors, equal to that which is accepted. The agreement would be even more striking if the combination of *s*-propyl radicals has a small positive activation energy. For $D(s\text{-}C_3H_7\text{—}H) = 97 - \frac{1}{2}E_1$. A value of E_1 of a few kcal mole^{-1} would also bring E_8 more into line with the assumed value of E_{-6}. The agreement between the values for the strength of the C—H bond can, however, only be obtained on the assumption that the rearrangement of the incipient ethylidene in the activated complex has no activation energy.

The negligible energy barrier for the decomposition *s*-propyl to ethylene suggests that the configuration of the activated complex is very similar to that of the complex for the decomposition of *n*-propyl. Hence the activated complexes for the addition of methyl to ethylene must be nearly identical irrespective

of whether *n*-propyl or *s*-propyl is ultimately formed. There are, indeed, some indications that the products of similar additions are formed in amounts determined more by the constants for the thermodynamic equilibria between the species than by kinetic considerations.

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661. *The Reactions of Methyl Radicals with Thiols.*

By J. A. KERR and A. F. TROTMAN-DICKENSON.

THE high reactivity of thiols with free radicals is well known; for this reason thiols are extensively used as chain-transfer agents in polymerisations. Little quantitative work on the kinetics of their reactions in solutions has been reported and still less appears to have been done on the gas phase. This Note records an attempt to investigate the kinetics of the attack of methyl radicals on thiols :

$$CH_3\cdot + RSH = CH_4 + RS\cdot \quad \ldots\ldots\ldots\ldots \quad (1)$$

The photolysis of acetone was used to provide methyl radicals. In general the procedure of Trotman-Dickenson and Steacie [1] was followed. Photolysis was carried out in a Pyrex vessel so that no light was absorbed by the thiols. The gases produced were analysed with a standard low-temperature distillation apparatus; carbon monoxide was oxidised over copper oxide.

During the photolysis methane, ethane, and carbon monoxide were produced by the following reactions :

$$CH_3\cdot CO\cdot CH_3 + h\nu = CH_3\cdot CO\cdot + CH_3\cdot \quad \ldots\ldots\ldots\ldots \quad (2)$$

$$CH_3\cdot CO\cdot = CH_3\cdot + CO \quad \ldots\ldots\ldots\ldots \quad (3)$$

$$CH_3\cdot + RSH = CH_4 + RS\cdot \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$CH_3\cdot + CH_3\cdot CO\cdot CH_3 = CH_4 + \cdot CH_2\cdot CO\cdot CH_3 \quad \ldots\ldots\ldots\ldots \quad (4)$$

$$2CH_3\cdot = C_2H_6 \quad \ldots\ldots\ldots\ldots \quad (5)$$

It can be shown that :

$$\frac{k_1}{k_5^{\frac{1}{2}}} = \frac{R_{CH_4} - (k_4/k_5^{\frac{1}{2}})[CH_3\cdot CO\cdot CH_3]R^{\frac{1}{2}}_{C_2H_6}}{R^{\frac{1}{2}}_{C_2H_6}[RSH]}$$

where the k's are the rate constants of the reactions and R_{CH_4} and $R_{C_2H_6}$ are the rates of formation of the products. Application of this equation involves a knowledge of k_4. The value of this rate constant is uncertain at less than 100° because methane is also formed by additional reactions, probably including the reactions of the acetyl radical.[2] The present experiments could not be carried out at temperatures as high 100° because the rate of reaction (1) was so great that it was impossible to obtain reproducible results. Accordingly all the rate constants were determined at 30°. The uncertainties in k_4 were unimportant because it is about one-thousand times less than k_1. The results obtained with the higher thiols were not very reproducible. The mean values of 10^{-7} (mole^{-1} cm.^{3} sec.$^{-1}$), based on the value of k_5 advocated by Shepp,[3] are :

MeSH 1·8; EtSH 3·5; Pr^{i}SH 4·1; Bu^{t}SH 5·9

This order of reactivity is the same as that deduced from the photodecomposition of acetaldehyde catalysed by thiols.[4] If $\log_{10} A$ (mole^{-1} cm.^{3} sec.$^{-1}$) for these reactions is of the order of 11·3, as it is for many reactions of methyl, then the activation energies of these reactions lie between 5·6 and 4·9 kcal./mole.

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THE UNIVERSITY, EDINBURGH. [*Received, April 1st*, 1957.]

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542. *The Decomposition of Nitramide in Anisole Catalysed by Aniline Derivatives.*

By G. C. Fettes, J. A. Kerr, A. McClure, J. S. Slater, C. Steel, and A. F. Trotman-Dickenson.

Decomposition of nitramide catalysed by primary, secondary, and tertiary aniline derivatives in anisole has been investigated between 7° and 55°. Activation energies for the catalytic coefficients have been determined. The catalytic coefficients at 25° are related to the activation energies by the expression

$$\log_{10} k_c\ (25°)\ (\text{mole}^{-1}\ \text{kg. min.}^{-1}) = 23{\cdot}2 - 1{\cdot}63E\ (\text{kcal. mole}^{-1})$$

The catalytic coefficients of a series of acidic or basic catalysts for a reaction are normally related to their respective dissociation constants by the Brönsted relation. In theoretical discussions of this kind of free-energy relation it is generally supposed that the difference in the catalytic power of the various catalysts can be attributed to the different activation energies of the fundamental protolytic reactions.[1] The temperature coefficients of comparatively few reactions catalysed by acids or bases have been measured. Consequently it is difficult to say whether there is any real basis for the supposition. Further, most of the reactions for which temperature coefficients have been measured have been studied in aqueous solution. It is known that ionic processes in aqueous solution frequently do not conform to the simplest types of energy relation. Accordingly it is not surprising that the results obtained with aqueous solutions do not often yield simple relations between the catalytic coefficients and activation energies.

This work was undertaken to obtain results in a solvent which does not readily form hydrogen bonds. The decomposition of nitramide was chosen because it has been very fully investigated and can easily be followed.[1] Anisole is a convenient solvent which can easily be sufficiently purified and in which a considerable amount of work has been done. Substituted anilines were chosen as catalysts because they have also been fairly fully studied.[1-4]

Experimental

Materials.—Anisole was dried ($CaCl_2$) and fractionated on an 18″ column packed with glass helices. Several batches were purified; all behaved similarly. Aniline derivatives were distilled over potassium hydroxide pellets under reduced pressure and stored in sealed containers. Nitramide was prepared by the method of Marlies, LaMer, and Greenspan [5] and stored in a refrigerator as a solution in anisole.

Apparatus and Procedure.—The runs were carried out in reaction vessels similar to those used by Bell and Caldin.[3] The faster runs were carried out in vessels with taps, the slower runs in sealed vessels. The vessels were placed in a glass-fronted thermostat maintained to $\pm 0{\cdot}02°$ and were agitated by percussion. Reaction mixtures were made up by weight. First, a convenient quantity of catalyst (or catalyst solution for the stronger bases) was weighed in a weighing bottle. Anisole, to make approximately 2 g. of mixture, was then added. Finally, 2 c.c. of nitramide solution were added immediately before the mixture was introduced into the reaction vessel.

The runs were followed by observing the increase in pressure of the evolved gas. First-order plots were then drawn, based on the pressure of gas after complete reaction. In the

slowest runs the reaction vessels were placed in a warm bath to bring the reaction to completion overnight. The rate constants were deduced from the observations taken during the first two half-lives of the reactions, after which some of the plots tailed off. The catalytic coefficients of the bases were found to be a function of the concentration of the solutions. The extrapolations devised by Bell and Trotman-Dickenson [3] were used to obtain the true coefficients.

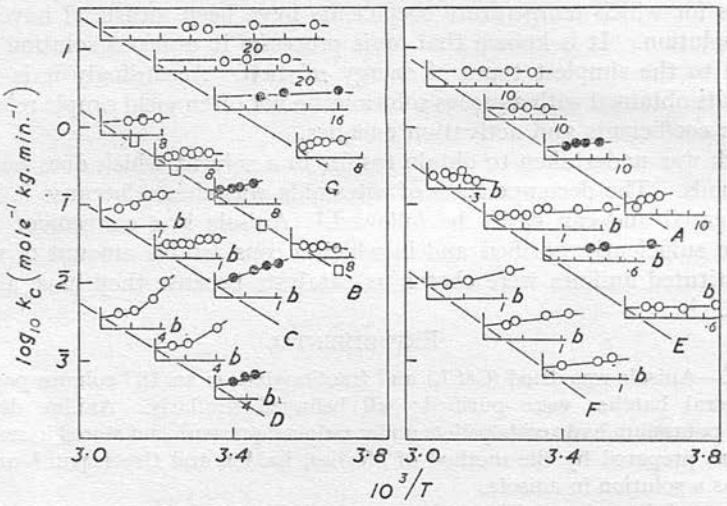
Results

The results of the kinetic measurements are included in Arrhenius plots (Fig. 1*a* and *b*) which show the catalytic coefficients from the individual runs and the extrapolations employed. The results are summarized in the Table. Generally they agree very well with those of Bell and Trotman-Dickenson [3] and Bell and Caldin,[2] those for *m*-chloroaniline being the only

Base	Catalytic coefficients, $10^3 k_c$ (mole^{-1} kg. min.$^{-1}$) (temp. in parentheses)				$\log_{10} A$	E (kcal. mole^{-1})
Diethyl-*p*-toluidine ...	480 (7·6°)	2295 (25·0°)	6760 (39·6°)	17,340 (54·1)°	9·43	13·9
Dimethyl-*p*-toluidine	105 (7·6)	599 (25·0)	1730 (39·6)	4875 (54·1)	9·22	14·5
Dimethylaniline	31 (8·6)	150 (25·0)	425 (40·0)	1230 (54·1)	8·81	14·8
Methylaniline	4·28 (7·7)	27·6 (25·0)	72·3 (40·0)	242 (54·1)	8·17	15·0
Aniline	—	8·07 (25·0)	30·0 (40·0)	80·0 (54·0	8·21	15·5
m-Chloroaniline	—	0·85 (25·0)	2·90 (39·6)	9·5 (54·1)	7·44	16·1
o-Chloroaniline	—	0·20 (25·0)	1·43 (40·0)	3·80 (54·1)	5·87	14·1

exceptions (we can suggest no reason for the discrepancy; the identity of the present material was confirmed by measurement of its refractive index and of the m. p. of its benzoyl derivative). The accuracy of the determination of the activation energies cannot be readily assessed because of the need for the extrapolation. An error of $\pm 0{\cdot}3$ kcal. mole^{-1} may reasonably be assigned.

FIG. 1*a and b*. *Arrhenius plots for the decomposition of nitramide in anisole catalysed by aniline derivatives. The individual points and the extrapolations are shown.* ○, *This work*; ●, *Bell and Trotman-Dickenson* [3]; □, *Bell and Caldin.*[2] *Concentrations are in moles kg.*$^{-1}$. *Except where the scale is marked b when the second method of extrapolation was used, the concentration scale on the abscissæ is for* $1/\sqrt{b}$ *corresponding to the first method of extrapolation. A, Dimethyl-*p*-toluidine; B, dimethyls aniline; C, aniline; D, o-chloroaniline; E, methylaniline; F, m-chloroaniline; G, diethyl-*p*-toluidine.*



Discussion

The activation energies of the catalytic coefficients are plotted against the catalytic coefficients of the various bases at 25° in Fig. 2. All except that for *o*-chloroaniline lie on a straight line given by $\log_{10} k_c\,(25°) = 23{\cdot}2 - 1{\cdot}63E$. The deviation of the *ortho*-substituted compound is not surprising; many free-energy relations break down for *ortho*-compounds. The slope of the line in Fig. 2 differs markedly from that which would be obtained (broken line) if all the differences between the catalytic coefficients could be attributed to variations in activation energy. The line representing the variation of $\log_{10} k_c$ with E deviates from

the " theoretical " slope, which corresponds to a constant value of A, for many series of reactions. Usually the slope is too great, *i.e.*, systematic changes in A compensate for the variations in E. In the present reaction the reverse occurs; A is not constant; it varies so as to reinforce the changes in E.

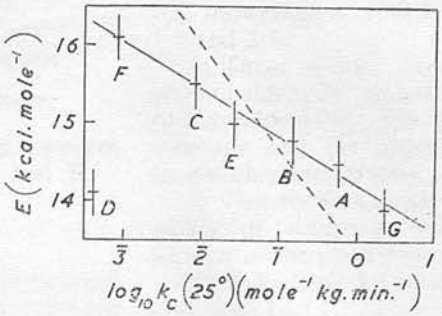


FIG. 2. *Relation between activation energies and catalytic coefficients for the aniline-catalysed decomposition of nitramide. A—G, see Fig. 1. Slope of broken line* $= 2{\cdot}303RT$.

The fact that the activation energies of the primary, secondary, and tertiary bases (except *o*-chloroaniline) obey the same relation supports the interpretation of the basic strength of amines, as measured in aqueous solutions, which has been suggested by Bell and Trotman-Dickenson.[3, 6]

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THE COMBINATION OF UNLIKE RADICALS IN THE GAS PHASE

By J. A. Kerr and A. F. Trotman-Dickenson

Chemistry Department, the University, Edinburgh

Three combination reactions can occur in a system containing two different free radicals, A and B:

$$2A = A_2 \quad .. \quad .. \quad k_{aa}$$
$$2B = B_2 \quad .. \quad .. \quad k_{bb}$$
$$A + B = AB \quad .. \quad .. \quad k_{ab}$$

According to the simple collision theory of chemical kinetics the ratio $k_{ab}/(k_{aa}k_{bb})^{\frac{1}{2}}$ should equal 2 if none of the reactions has an activation energy. It has long been known that the reactions that terminate polymerisations and autoxidations in solution deviate from this simple relation. Recently several measurements of the ratio have been reported for gaseous systems. Further information may be deduced from other published results and we have determined the ratio for ethyl and propyl radicals.

The present position is indicated in the Table which may be augmented by a few notes on the means by which the results were obtained:

The Combination of Unlike Radicals in the Gas Phase

Radicals A	Radicals B	$k_{ab}/(k_{aa}k_{bb})^{\frac{1}{2}}$	Reference
Methyl	Ethyl	1·9	1 *a*
		2·0	2
Methyl	*n*-Propyl	2·6	3 *b*
Methyl	Methoxyl	1·9	4
Methyl	Acetyl	1·7	4
Methyl	Acetonyl	1·5	5 *c*
Ethyl	*n*-Propyl	1·9	6 *d*
Ethyl	*s*-Propyl	2·05	6 *d*
		2	7 *e*
Ethyl	*n*-Heptafluoropropyl	3·2	8 *f*
Ethyl	Pentanonyl	1·7	9

(*a*) This figure has been calculated by us from the results on the photolysis of methyl ethyl ketone below 170°C. The amount of ethane formed by methyl combination was calculated from the yield of methane and from the rate constant for the attack of methyl radicals on the ketone. This constant had been found by photolysing azomethane mixed with the ketone.[1]

(*b*) This result is based on a few runs which were not very concordant; the limits of error are large.

(*c*) The authors reported very scattered results that showed no trend but the error limits were between 1·0 and 2·5.

(*d*) These results were obtained by photolysing propionaldehyde mixed with *n*-butyraldehyde or *iso*butyraldehyde. The products were analysed for *n*-butane and the appropriate pentane and hexane by gas chromatography.

(*e*) This result has been calculated by us from the yields of *n*-butane, *iso*pentane and di-*iso*propyl formed in the photolysis of *iso*propyl propionate.

(*f*) Calculated by us from the yields of *n*-butane and *n*-1 : 1 : 1 : 2 : 2 : 3 : 3-heptafluoropentane. The yield of perfluorohexane was estimated as was done by the original authors for the photolysis of di-*n*-perfluoropropyl ketone in the presence of ethane. The figures are rather scattered.

None of the ratios vary with temperature. Only the ratio involving perfluoropropyl differs significantly from the expected value of two and its deviation is smaller than might have been expected for such a polar radical. The results must therefore be regarded as an indication, though not as a proof, that all these combinations occur on every collision. It is probable, however, that the collision diameter required for the present purpose is generally slightly different from that required for the calculation of transport properties, as it is known to be for the combination of two methyl radicals.[10]

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